

The University of Chicago

THE HEATS OF MIXING OF AQUEOUS
SOLUTIONS OF NON-REACTING
STRONG ELECTROLYTES

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

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MARTIN BRISTOW SMITH

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INTRODUCTION

The total ionic strength μ of a solution may be defined as the sum of the ionic strengths of all the kinds of ions present, where the ionic strength μ_i of the i th kind of ion is defined as the product of one-half the molality of the ion by the square of the charge of the ion. Symbolically,

$$\mu = \sum_i \mu_i, \quad (1)$$

$$\text{where } \mu_i = \left(\frac{m_i}{2}\right) z_i^2. \quad (2)$$

It can be demonstrated easily (see "Definitions and Propositions," no. 6) that if an arbitrary number of solutions of non-reacting strong electrolytes having the same ionic strength (weight basis) are mixed in arbitrary proportions, the resulting solution will have that same ionic strength; and, conversely, that any solution containing strong electrolytes can be prepared by mixing appropriate quantities of solutions of the individual electrolytes having the same ionic strength.

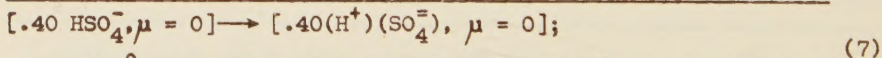
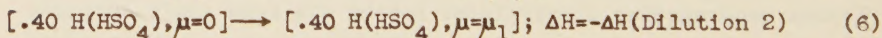
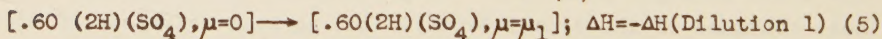
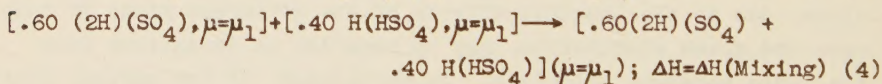
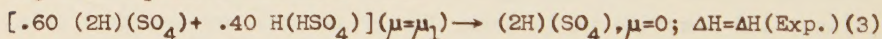
Lewis and Randall¹ discovered empirically, and Debye and Hückel² justified theoretically, the significant fact that in dilute solutions the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength. From this result, it seems reasonable to form the hypothesis that other properties of a given strong electrolyte are primarily dependent on the ionic strength of the solution at all concentrations; and that the variations, larger in more concentrated solutions, due to the specific effects of the different kinds of ions upon the given electrolyte, may be regarded as deviations from the ionic strength principle. In particular, if the partial molal heat contents of the constituents of two aqueous solutions of different non-reacting electrolytes having the same ionic strength were invariant at that total ionic strength, then no heat would

¹Lewis and Randall, "Thermodynamics," The McGraw-Hill Book Co., 1923, chap. xxviii.

²Debye and Hückel, Physik. Z., 24, 185 (1923).

be liberated when the two solutions were mixed; for the heat content of the mixture would be equal to the sum of the heat contents of the solutions before mixing. In actual experiments we should expect to obtain small heat effects whose magnitudes decrease rapidly as the ionic strength is decreased. One of the objectives of this research is to test this prediction and to determine whether deviations from it can be correlated with other properties of the ions.

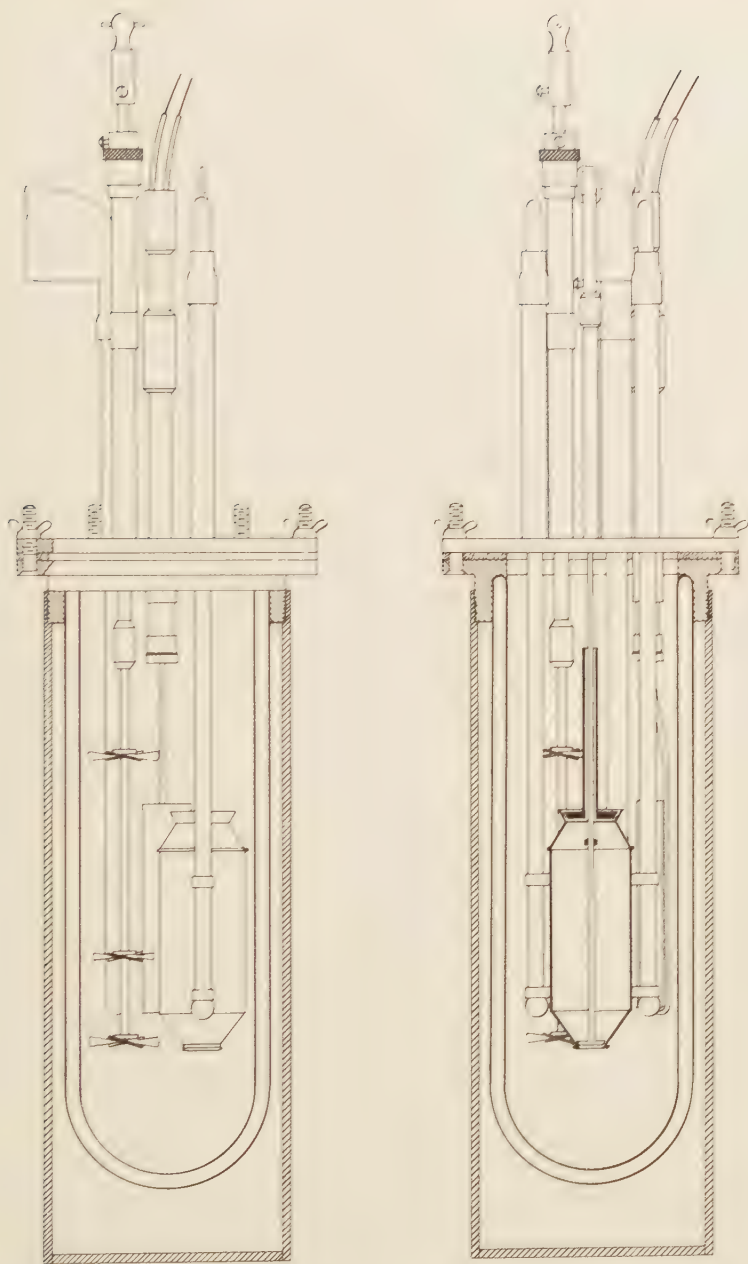
The heat of mixing of solutions of non-reacting strong electrolytes having the same ionic strength is encountered in the calculation of ΔH° of ionization of weak electrolytes from calorimetric data. Singleterry,³ in calculating ΔH° of ionization of the HSO_4^- ion, assumed that "in a mixture of electrolytes the heat of dilution of each constituent is a function only of the total ionic strength of the solution," stating that "for dilute solutions it seemed a reasonable first approximation." His assumption is equivalent to the assumption that the heat of mixing of solutions of non-reacting strong electrolytes of the same ionic strength is zero. To illustrate the role of the heat of mixing in the computation of ΔH° of dissociation, suppose that the HSO_4^- ion in a certain solution of sulfuric acid is 60 per cent dissociated and that an experiment is performed in which a measured quantity of this solution is diluted with a very large amount of water, the heat of the process being measured. Let $(2\text{H})(\text{SO}_4)$ represent completely dissociated sulfuric acid and let $\text{H}(\text{HSO}_4)$ represent H^+ ion and undissociated HSO_4^- ion. We now write the following four equations and add them:



$$\Delta H = .40 \Delta H^\circ(\text{Dissociation}) = \Delta H(\text{Exp.}) + \Delta H(\text{Mix.}) - \Delta H(\text{Dil.1}) - \Delta H(\text{Dil.2})$$

$$\Delta H^\circ(\text{Diss.}) = (1/.40)[\Delta H(\text{Exp.}) + \Delta H(\text{Mix.}) - \Delta H(\text{Dil.1}) - \Delta H(\text{Dil.2})]. \quad (8)$$

³Singleterry, Ph. D. Dissertation, University of Chicago, 1940.



THE CALORIMETER

Thus, ΔH° of dissociation is expressible in terms of heats of dilution and a hypothetical heat of mixing at constant ionic strength. One can approximate this hypothetical quantity by carrying out a suitably chosen actual experiment, for example by mixing sodium sulfate and sodium chloride at the same ionic strength, μ_1 . The complete calculation of the ΔH° of dissociation of a weak electrolyte, then, necessitates a study of the heats of mixing of solutions of non-reacting strong electrolytes of the same ionic strength.

The calculation of the heat of dilution of salt mixtures is another problem to which the "heat of mixing" may be applied. If the heats of dilution of salt A and of salt B are known, as well as the heat of mixing, the heat of dilution of any mixture of A and B, say the 1-1 mixture, can be computed. For the case in which both A and B are 1-1 salts, and dilutions from $\mu=5$ to $\mu=1$ are considered, we may write:

$$.5 A(\mu=5) \rightarrow .5 A(\mu=1); \Delta H = \Delta H(\text{Dilution A}) \quad (9)$$

$$.5 B(\mu=5) \rightarrow .5 B(\mu=1); \Delta H = \Delta H(\text{Dilution B}) \quad (10)$$

$$.5 A(\mu=1) + .5 B(\mu=1) \rightarrow \text{Mixture } (\mu=1); \Delta H = \Delta H(\text{Mixing}, \mu=1) \quad (11)$$

$$\text{Mixt. } (\mu=5) \rightarrow .5 A(\mu=5) + .5 B(\mu=5); \Delta H = \Delta H(\text{Mixing}, \mu=5) \quad (12)$$

Upon adding equations (9), (10), (11), and (12), we obtain:

$$\text{Mixture } (\mu = 5) \longrightarrow \text{Mixture } (\mu = 1);$$

$$\Delta H = \Delta H(\text{Dilution of Mixture}) \quad (13)$$

$$= \Delta H(\text{Dil. A}) + \Delta H(\text{Dil. B}) + \Delta H(\text{Mix.}, \mu=1) - \Delta H(\text{Mix.}, \mu=5) \quad (13a)$$

Thus, the heat of dilution of the salt mixture may be expressed in terms of the heats of dilution of the individual salts and the heats of mixing at the two ionic strengths.

A fourth and self-sufficient reason for the investigation of the heat of mixing is that the knowledge obtained would be useful in itself. It is desirable to know which method of expressing the concentration provides the basis upon which the heats of mixing are smallest.

APPARATUS

The apparatus used was essentially that developed by Dr. T. F. Young and his co-workers for the measurement of heats of dilution. Hence, more detailed descriptions of most parts of the apparatus may be found in the theses⁴ of these co-workers, and in

⁴Ph. D. Dissertations, University of Chicago, by (a) Vogel, 1930; (b) Groenier, 1931; (c) Machin, 1932; and (d) Buck, 1935.

the published papers.⁵

Calorimeter

The calorimeter, of the submerged-chamber type, consisted of a silvered cylindrical Dewar flask of 1050 cc. capacity cemented by means of litharge-glycerin cement into a brass ring to which the calorimeter top could be bolted. The ring was threaded on the outside so that it could be screwed tightly into a cylindrical brass can threaded on the inside and just large enough to contain the Dewar. This can protected the Dewar, supported it in an upright position when the calorimeter was outside the bath, and greatly reduced the chance of water leaking in through the cement joint during an experiment. The brass calorimeter top was provided with six chimneys to accommodate the auxiliary parts, namely, the two glass rods which supported the dilution vessel, the tantalum rod which opened the valves of the dilution vessel, the stirrer, the heater, and the thermel. Stretched over the tops of the chimneys were short pieces of rubber tubing which fitted the auxiliary parts and thus made the apparatus vapor-tight. A gasket cut from rubber sheet 1/8 inch thick supplied by the Garlock Packing Company was used at the joint when the top and bottom halves of the calorimeter were bolted together.

Dilution Pipet

The dilution pipet, made of tantalum and having a capacity of 75 cc., was designed and described by Buck.⁶ Vaseline, thinned with mineral oil and applied to the pipet valve-seats with a camel's-hair brush, made the pipet liquid-tight. A simple device made it unnecessary to remove a wall of the thermostat when the pipet was opened during an experiment. This device consisted of a thin wire which led from the top of the pipet rod, to which it was fastened, over a pulley, through an opening in the thermostat wall, and to the outside. The pipet opened smoothly, and remained open, when a ring at the free end of the wire was pulled gently and then secured on a properly located pin.

⁵(a) Young and Vogel, J. Am. Chem. Soc., 54, 3030 (1932);
(b) Young and Machin, J. Am. Chem. Soc., 58, 2254 (1936).

⁶Loc. cit.

Stirrer

The stirrer, also of tantalum, was cemented into a glass tube in order to diminish heat leakage. It was rotated by a small synchronous motor at the rate of 450 revolutions per minute.

Thermel

The temperature-measuring device was a copper-constantan U-shaped thermel having 24 junctions at each end. The copper wire was No. 32, and the constantan No. 24, Brown and Sharpe gauge. The working end of the thermel extended into the calorimeter through the proper chimney. The reference end extended through a sleeve and a ring, both made of a cast phenolic resin, into a silvered pear-shaped Dewar. The sleeve, attached loosely to the thermel so that it could be made to rotate or slide upward easily, screwed into the ring, which was cemented onto the Dewar with litharge-glycerin. The Dewar and ring were supported in the bath by means of clamps and a brass rod of square cross-section, in such a manner that they were constrained to move in one vertical line as long as the positions of the clamps were not changed. Since the calorimeter was always mounted in exactly the same position, the thermel and sleeve were confined always to the same vertical line. Therefore, the Dewar and ring remained in alignment with the thermel and sleeve. The length of the sleeve, 5 inches, was such that the top projected above the surface of the bath. A disc of thick hard rubber fitted tightly around the thermel just above the sleeve and was brought down flush with the top of the sleeve after the reference Dewar was attached. This system of Dewar, ring, sleeve, and disc replaced the system of Dewar and split cork used by previous workers.

Heater

The heater resembled the one described by Groenier.⁷ It consisted of a coil of No. 40 constantan wire wound around a strip of mica. Thin sheets of mica on both sides of the coil served to insulate it from the platinum case. A long, thin platinum-iridium tube carried the No. 26 copper lead wires and supported the heater in the calorimeter. When the heater was repaired at the beginning

⁷Loc. cit.

of the work, one lead wire became shorted to the case. Lest the other lead also become shorted, the tube was not bent into a U as recommended by Groenier, although this meant an increase in heat loss up the tube during the heating period. Care was taken that the shorted lead always be connected to the grounded side of the heater circuit.

Thermostat

The thermostat consisted of a water-filled tank whose dimensions were 76x76x61 cm. A space above the tank, 67 cm. high, was enclosed by pieces of celotex which were removable on three sides. The thermostat temperature was maintained by a large mercury-in-glass regulator operating a relay which controlled a 250 watt heating lamp. To assist in the regulation of the temperature, cold water was passed through a copper coil of the proper size immersed in the bath. The correct size of coil varies widely with conditions of room temperature and humidity and temperature of cooling water, even though the bath be used only at 25°. A short-range thermometer, graduated in hundredths, which had been compared with a Bureau of Standards thermometer was used to read the bath temperature. Except for experiments at temperatures other than 25°, the thermostat temperature was kept in the neighborhood of 24.80° C. since the heat of stirring contributed about 0.20° C. to the calorimeter temperature, which was thus within a few hundredths of a degree of 25.00° C. at the beginning of each experiment.

Measuring Instruments and Thermel Circuit

A White double potentiometer, built by Leeds and Northrup Company, was used to measure the electromotive force of the thermel and the potential differences across the standard resistances of the heater circuit. The range of this potentiometer was 0.01 volt. The working currents were adjusted against an Eppley standard cell. The type-HS galvanometer, also made by Leeds and Northrup Company, was mounted four meters from the scale. Its sensitivity varied between 15 and 20 mm. per microvolt. The electrical measuring circuit was entirely of copper and was carefully shielded and grounded. The galvanometer leads were crossed at intervals, as were the thermel leads, in order that stray electromotive forces arising in these circuits from fluctuations in the

magnetic fields might cancel. A reversing switch in the thermel circuit made it unnecessary to interchange the connections inside the thermostat when the thermel EMF passed through zero.

Heater Circuit

The heater circuit consisted essentially of a standard 0.1 ohm resistance and either the heater or the auxiliary resistance, in parallel with a standard 1 ohm resistance and a standard 10,000 ohm resistance, current being supplied from a 50 volt bank of storage batteries. The terminals of the standard 0.1 ohm resistance and also those of the standard 1 ohm resistance were connected to the potentiometer so that the potential differences across these resistances could be measured. By means of a system of switches and a precision clock driven by weights, current could be passed through the heater for an exactly integral number of seconds.

Weight Pipets

Weight pipets fitted with ground glass stoppers and tip caps were used in the weighing out of solutions. The two large pipets each had a capacity of about 1025 cc. The two small ones had capacities of 76 cc. and 92 cc., respectively.

PREPARATION AND ANALYSIS OF SOLUTIONS

The salts used, namely sodium chloride, anhydrous sodium sulfate, potassium chloride, lithium chloride, sodium bromide, sodium nitrate, and potassium nitrate were Mallinckrodt Analytical Reagents. The hydrochloric acid was the Merck C.P. Reagent.

Solutions of sodium chloride and of sodium sulfate were prepared from the solid salts, the bottles containing the salts having previously been shaken thoroughly. Solutions used in the determination of heats of mixing of sodium chloride with sodium sulfate were made up to exactly integral ionic strengths, the salts being temporarily assumed to be 100 per cent pure; subsequently, the true compositions of the salts were determined by analysis and the true ionic strengths were calculated. In the preparation of solutions of sodium chloride and of sodium sulfate used in experiments other than determinations of the heats of mixing of sodium chloride with sodium sulfate, the true compositions

of the salts were taken into account.

Solutions of potassium chloride, of lithium chloride, of hydrochloric acid, of sodium bromide, of sodium nitrate, and of potassium nitrate were prepared by dilution of concentrated stock solutions which had been analyzed.

The solutions were prepared by weight as needed, a liter at a time. All solutions used in heat of mixing experiments were made up to exactly integral ionic strengths (the reader is referred to par. 2 of this section) as follows: a clean, dry one-liter flask provided with a cork (either wrapped in tin foil or coated with paraffin) was weighed. The salt or stock solution was introduced and its weight in vacuo determined, from which the weight of water needed and the correct final total weight in air were computed. An amount of distilled water slightly less than the calculated amount was then added by graduate; and, with the flask on the balance pan, water was carefully added by means of a dropper until the flask and contents weighed within 0.02 gram of the correct amount. Solutions used in heat of dilution experiments were prepared in the same manner except that the operations with the dropper were omitted since the ionic strengths did not have to agree exactly with predetermined values.

The sodium sulfate was analyzed by the residue method of Richards and Hall.⁸ Duplicate analyses agreed within 0.06%. The sodium chloride was analyzed by the residue method and also by the silver chloride precipitation method as described by Pierce and Haenisch.⁹ Duplicate analyses by the residue method agreed within 0.08%. Duplicate analyses by the precipitation method agreed within 0.06%. The average result for the residue method differed by less than 0.02% from the average result for the precipitation method.

The stock solutions of potassium chloride, of lithium chloride, of sodium bromide, of sodium nitrate, and of potassium nitrate were analyzed by the residue method. The stock solutions of lithium chloride and of hydrochloric acid were analyzed by the silver chloride precipitation method. For the potassium chloride stock solution, the maximum discrepancy among the four duplicate

⁸Richards and Hall, J. Am. Chem. Soc., **51**, 709 (1929).

⁹Pierce and Haenisch, "Quantitative Analysis," John Wiley & Sons, Inc. (1937), p. 274.

analyses was 0.05%. Duplicate analyses of the lithium chloride stock solution by the residue method agreed within 0.02%; duplicate analyses by the precipitation method agreed within 0.04%. The average result for the residue method differed by less than 0.06% from the average result for the precipitation method. These examples are typical of the results obtained.

THE EXPERIMENTAL METHOD

The most direct method for the determination of the heat of mixing of two electrolytic solutions over the entire composition range would involve the measurement in a calorimeter of the heat liberated or absorbed when the solutions are mixed in different proportions. However, due to limitations in the construction of apparatus, this is impossible at present since the ratio of the volume of the dilution pipet to the volume of liquid in the Dewar cannot be made appreciably greater than 1/9. Hence, a less direct method must be chosen.

One method, used by Parker,¹⁰ involved the mixing of solutions of different ionic strengths. The two ionic strengths were so chosen, and the proportions were so adjusted, that a predetermined total ionic strength was obtained after mixing. This heat effect was "corrected" for the heat of dilution (or of concentration) of each salt from its initial ionic strength to the final total ionic strength. The figure so obtained was the heat of mixing at the final total ionic strength and a certain solute-fraction. By variation of the initial ionic strengths, the final total ionic strength being kept constant, it was possible to determine the heat of mixing over a considerable portion of the solute-fraction range, the size of the portion being determined by the solubilities of the solutes and the total ionic strength. However, the method was unsatisfactory for several reasons. It required an accurate knowledge of the heats of dilution of both solutes. The large corrections necessary made the results uncertain. In addition, the experiments were too cumbersome and the calculations consumed too much time.

¹⁰Parker, Master's thesis, University of Chicago, 1940.

The method employed throughout this research was essentially direct since each experiment involved the mixing of two solutions of the same ionic strength. At the beginning of a series of experiments in the heats of mixing of solutions of solute A and solute B at an ionic strength of μ_1 , a liter of the aqueous solution of each solute was prepared. In the first experiment, about 73 cc. of solution A in the pipet was mixed with about 660 cc. of solution B in the Dewar. In the second experiment, about 73 cc. of solution A was mixed with about 660 cc. of the solution produced in the first experiment. In the third experiment, about 73 cc. of solution A was mixed with about 660 cc. of the solution from the second experiment, etc. The solution thus became continually richer in solute A and, at the end of six experiments, was nearly as rich in A as in B. This series was then discontinued and a new series of six experiments started in which solution B in the pipet was mixed in the first experiment with solution A and in each subsequent experiment with the solution produced in the preceding experiment. Two liters of solution A and two liters of solution B sufficed for an entire set of twelve experiments.

EXPERIMENTAL PROCEDURE

With the various parts of the apparatus in working condition and the calorimeter clean and dry, an experiment was begun by the application of vaseline to the valve-seats of the dilution vessel, the upper and lower valves being supported in elevated positions by a small clothespin and a screw clamp, respectively. The lower valve was then seated properly, the upper valve remaining above its seat to permit the introduction of the solution. One of the small weight pipets was rinsed with the proper solution, 75 cc. was added by graduate, and the pipet was weighed to the nearest milligram. The contents of the pipet were allowed to drain into the dilution vessel, which was then sealed by the seating of the upper valve and the application of vaseline to the space between the rod and the sleeve. The pipet was reweighed. One of the large weight pipets was rinsed with the other solution, whose temperature was then adjusted to such a value in the range 22-25°C. (this value depended upon the room temperature) that the calorimeter, after being assembled and placed in the thermostat,

would be $0.2-0.6^{\circ}$ cooler than the bath. The solution was transferred to the pipet and the pipet weighed to the nearest centigram. The solution was allowed to drain into the Dewar until the surface of the liquid had risen to the end of a wire suspended from the top of the Dewar. This volume of solution, about 660 cc., was such that the ratio of the volumes of the solutions used, and therefore the ratio of the weights of water, was always near 9/1. The pipet was set aside to be weighed later. If the dilution vessel had not leaked, the calorimeter was quickly assembled and placed in position in the thermostat. The stirring mechanism was attached, electrical connections were made at the thermel and the heater, the wire for opening the dilution vessel was attached, and the stirring was begun.

The thermel EMF was then read on the P dials of the potentiometer; and, since the temperature of the calorimeter was below that of the thermostat by 200-600 microvolts (as a result of the adjustment of the temperature of the solution used in the Dewar), current was passed through the calorimeter heater until the equilibrium temperature was reached. This temperature was 150-225 microvolts above the temperature of the thermostat because of the heat of stirring, the exact value depending principally upon the viscosity of the solution. The temperature of the bath was read. The reference Dewar was raised into position and the effect of this operation on the thermel reading noted. If, as was usually the case, the thermel reading was not changed more than two microvolts (0.002 degree), the thermel sleeve was screwed tightly into the ring of the Dewar, the water that was forced upward between thermel and sleeve by this operation absorbed by means of paper tissue, and the disc placed in position on top of the sleeve. If, however, the thermel reading was changed more than two microvolts, the reference Dewar was lowered and three or four liters of bath water siphoned through it. It was then raised into position again, the effect on the thermel reading noted, etc. The walls of the thermostat were closed and kept closed until the experiment was completed. To steady the heater current for the electrical calibration of the calorimeter, the current was allowed to pass through an auxiliary resistor whose resistance was equal to that of the heater. The calorimeter was allowed to approach equilibrium with the bath until a steady thermel drift of not more than 0.02 micro-

volt per minute was observed, two hours usually sufficing.

Before the actual experiment was started, the working currents of the potentiometer were adjusted against the standard cell, and then the sensitivity of the galvanometer in the thermel circuit was determined. The thermel EMF was observed at minutely intervals, recorded, and plotted against the time. Readings were taken for about twelve minutes and, thirty seconds after the last observation, the dilution pipet was opened. The drift of the thermel EMF was again observed for a period of about twelve minutes. Thirty seconds after the last observation, a calibration heating period lasting exactly three minutes was begun. At the middle of the period, the strength of the current passing through the heater was determined by measurement on the Q dials of the fall of potential across the standard 0.1 ohm resistance in series with the heater. At the end of the period, the thermel readings were resumed for about twelve minutes, and then current was again passed through the heater for a period of exactly 180 seconds. A final series of about twelve readings was taken.

The resistance of the heater was determined at the end of each experiment by the almost simultaneous measurement of the voltage drop across the standard 0.1 ohm resistance (the "Q" reading) and that across the standard 1 ohm resistance (the "P" reading). The resistance was calculated from the relation

$$R = 1000.0 (P/Q). \quad (14)$$

The microvolt change for the mixing and that for each of the two heating periods were obtained from the plot of EMF versus time, in which each of the four sections of the experiment was plotted on a separate large scale of ordinate, the method of extrapolation described by Vogel¹¹ being used.

The energy in 15° calories supplied to the calorimeter during each heating period was computed from the equation,

$$\text{Energy} = 4.3011(P \times 10^{-3})^2(R \times 10^{-3}), \quad (15)$$

which was derived from the fundamental relation

$$\text{Energy} = \frac{I^2 R t}{4.185} \quad (16)$$

for the special case of these experiments, in which t , the time, = 180 seconds and I , the current, = $P \times 10^{-5}$ amperes. R is the resistance of the heater in ohms and 4.185 the number of joules per

¹¹Loc. cit.

15° calorie.¹² The heat capacity in calories per microvolt for each heating calibration was calculated by division of the energy input by the microvolt rise. The heat capacities from the duplicate electrical calibrations always agreed with 0.1%.

The value of ΔH in calories for the mixing was calculated by multiplication of the microvolt change for the mixing by the average heat capacity in calories per microvolt.

The temperature of the calorimeter at the instant of mixing was determined by addition to the bath temperature of the product of the thermel reading in microvolts and the reciprocal of the power of the thermel (0.00104 degrees per microvolt).

Finally, the calorimeter was removed from the bath and dismantled. If the solution was to be used in the next experiment, it was carefully poured into a flask, which was then stoppered. The calorimeter parts were freed from vaseline, rinsed several times with water and once with ethyl alcohol, and dried by means of an air stream.

DEFINITIONS AND PROPOSITIONS

For the material which is to follow, it will be convenient to define a few terms and symbols and to discuss certain relations among them.

1. Definition. Any solute which is 100% dissociated in aqueous solutions of moderate concentration (say $\mu = 1$) will be termed a proper solute.

2. Definition. Given a proper solute of formula weight $\overline{FW}$, one molecule of which will dissociate into the set of ions

$$\sum_j x_j I_j^{z_j} = x_1 I_1^{z_1} + x_2 I_2^{z_2} + \dots, \text{ where} \quad (17)$$

(a) $I_j^{z_j}$ is an ion of the j th kind,

(b) x_j = number of $I_j^{z_j}$'s per molecule of solute, and

(c) z_j = charge on $I_j^{z_j}$;

the strionic weight of the solute is defined as

$$\overline{SW} = \frac{\overline{FW}}{\sum_j \left(\frac{x_j}{2}\right) z_j^2} \quad (18)$$

¹²Bichowski and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Co., New York, 1936.

3. Definition. One strion of a solute is defined as the strionic weight of the solute expressed in grams. Representing by $\underline{s}$ the number of strions contained in a given weight $\underline{W}$ of solute, we write:

$$s = \frac{W}{SW} \quad (19)$$

4. Definition. In a solution containing two solutes A and B:

(a) s_A = number of strions of solute A.

s_B = number of strions of solute B.

(b) $s = s_A + s_B$ = total number of strions.

(c) $S_A = \frac{s_A}{s} = \underline{\text{strion fraction}}$ of solute A.

$S_B = \frac{s_B}{s} = \text{strion fraction of solute B.}$

5. Proposition. In aqueous solutions containing non-reacting proper solutes, the ionic strength equals the number of strions of solute per kilogram of water.

Ionic strength has been defined (see eqs. (1) and (2)) as

$\mu = \sum_j \left(\frac{m_j}{2}\right) z_j^2$. Suppose a solution of ionic strength μ contains $\underline{W}$ grams of a single solute dissolved in $\underline{K}$ kilograms of water, and suppose the gross molality is $\underline{m}$. Then

$$m_j = x_j m \quad (20)$$

$$\mu = \sum_j \left(\frac{m_j}{2}\right) z_j^2 = \sum_j \left(\frac{x_j m}{2}\right) z_j^2 = m \sum_j \left(\frac{x_j}{2}\right) z_j^2 = \frac{W}{KFW} \cdot \sum_j \left(\frac{x_j}{2}\right) z_j^2 \quad (21)$$

$$= \frac{W}{K} \cdot \frac{\frac{FW}{\sum_j \left(\frac{x_j}{2}\right) z_j^2}}{FW} = \frac{W}{KSW} = \frac{s}{K} \quad (21a)$$

For a solution containing more than one solute, the total ionic strength is the sum of the ionic strengths of the individual solutes and this is easily seen to be the total number of strions of solute per kilogram of water.

6. Proposition. If an arbitrary number of solutions of proper solutes (non-reacting) having the same ionic strength (weight basis) are mixed in arbitrary proportions, the resulting solution will have that same ionic strength. Conversely, any solution containing proper solutes can be prepared by mixing appropriate quantities of solutions of the individual solutes having the same ionic strength.

To prove this proposition, we formulate the solutions of individual solutes as follows:

$$\text{Soln.}_1 = s_1 \text{ strions solute}_1 + k_1 \text{ kg. H}_2\text{O}; \mu_1 = s_1/k_1 \quad (22)$$

$$\text{Soln.}_2 = s_2 \text{ strions solute}_2 + k_2 \text{ kg. H}_2\text{O}; \mu_2 = s_2/k_2 \quad (23)$$

$$\vdots$$

$$\text{Soln.}_i = s_i \text{ strions solute}_i + k_i \text{ kg. H}_2\text{O}; \mu_i = s_i/k_i \quad (24)$$

It is given that $\frac{s_1}{k_1} = \frac{s_2}{k_2} = \frac{s_3}{k_3} = \dots = \frac{s_i}{k_i} = \dots$ Hence:

$$s_1 k_1 = k_1 s_1 \quad (25)$$

$$s_1 k_2 = k_1 s_2 \quad (26)$$

$$s_1 k_3 = k_1 s_3 \quad (27)$$

$$\vdots$$

$$s_1 k_i = k_1 s_i \quad (28)$$

Upon adding these equations, we obtain:

$$s_1(k_1 + k_2 + k_3 + \dots + k_i + \dots) = k_1(s_1 + s_2 + s_3 + \dots + s_i + \dots) \quad (29)$$

We formulate the final solution, after mixing, as follows:

$$\text{Soln.} = s \text{ strions solute} + k \text{ kg. H}_2\text{O}; \mu = \frac{s}{k} \quad (30)$$

$$\text{Then } s = \sum_i s_i; \quad (31)$$

$$k = \sum_i k_i. \quad (32)$$

$$\text{Hence, } s_1 k = k_1 s, \quad (33)$$

$$\text{whence } \frac{s}{k} = \mu = \frac{s_1}{k_1} = \mu_1; \quad (34)$$

$$\text{or } \mu = \mu_1 = \mu_2 = \mu_3 = \dots = \mu_i = \dots, \text{ qed.} \quad (35)$$

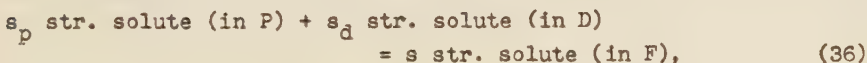
The converse is equally easy to establish.

7. Definition. A solution will be termed mono-solute, di-solute, or poly-solute according as it contains one, two, or more than two solutes.

8. Definition. The heat of mixing per strion for any actual experiment performed at constant ionic strength will be designated as $\Delta H/s$ for that experiment.

9. Definition. For a given di-solute solution, Q equals ΔH (not necessarily obtained directly by experiment) for the preparation of one strion of the solution (the amount of solution containing one strion of solute) by the mixing of mono-salt solutions of the same ionic strength.

10. Definition. A generalized mixing experiment may be formulated as follows:



- where (a) s_p = number of strions of solute in the pipet.
 s_d = number of strions of solute in the Dewar.
 (b) P = Pipet solution (before mixing).
 D = Dewar solution (before mixing).
 F = Final solution (after mixing).

In addition, we define

$$(c) S_p = \frac{s_p}{s_p + s_d} = \frac{s_p}{s}.$$

$$S_d = \frac{s_d}{s}.$$

- (d) S_{AD} = strion fraction of solute A in the Dewar Solution.
 S_{BD} = strion fraction of solute B in the Dewar Solution.
 S_{AF} = strion fraction of solute A in the Final Solution.
 S_{BF} = strion fraction of solute B in the Final Solution.

11. Definition. In a series of experiments, the letter i , used as suffix or subscript, will refer to the i th experiment in the series. In this notation, the series of experiments in which a solution of A in the pipet is mixed with solutions of the same ionic strength μ_1 (containing various proportions of A and B) in the Dewar can be formulated thus:

$$S_{p1} \text{ str. } A(\mu=\mu_1) + S_{d1} \text{ str. } B(\mu=\mu_1) = 1 \text{ str. } (A, B)(F1; \mu=\mu_1);$$

$$\Delta H = \left(\frac{\Delta H}{s}\right)_1 = Q_{F1} \quad (37)$$

$$S_{p2} \text{ str. } A(\mu=\mu_1) + S_{d2} \text{ str. } (A, B)(F1; \mu=\mu_1) = 1 \text{ str. } (A, B)(F2; \mu=\mu_1);$$

$$\Delta H = \left(\frac{\Delta H}{s}\right)_2 \quad (38)$$

$$S_{p3} \text{ str. } A(\mu=\mu_1) + S_{d3} \text{ str. } (A, B)(F2; \mu=\mu_1) = 1 \text{ str. } (A, B)(F3; \mu=\mu_1);$$

$$\vdots \quad \Delta H = \left(\frac{\Delta H}{s}\right)_3 \quad (39)$$

$$S_{pi} \text{ str. } A(\mu=\mu_1) + S_{di} \text{ str. } (A, B)[F(i-1); \mu=\mu_1] = 1 \text{ str. } (A, B)(Fi; \mu=\mu_1);$$

$$\Delta H = \left(\frac{\Delta H}{s}\right)_i \quad (40)$$

12. Proposition. The desired quantity Q (see Definition 9) for the final solution obtained in the i th mixing is given by the relation

$$Q_{Fi} = \left(\frac{\Delta H}{s}\right)_i + S_{di} Q_{Di}. \quad (41)$$

For we can write:

$$S_{ADi} \text{ str. } A(\mu=\mu_1) + S_{BDi} \text{ str. } B(\mu=\mu_1) = 1 \text{ str. } (A, B)(Di; \mu=\mu_1);$$

$$\Delta H = Q_{Di} \quad (42)$$

Multiplying the equation through by S_{di} and adding it to the equation for the i th mixing, we obtain the desired result:

$$S_{pi} \text{ str. A}(\mu=\mu_1) + S_{di} \text{ str. (A, B)}(Di:\mu=\mu_1) = 1 \text{ str. (A, B)}(Fi:\mu=\mu_1);$$

$$\Delta H = \left(\frac{\Delta H}{s}\right)_i \quad (43)$$

$$S_{di} S_{Adi} \text{ str. A}(\mu=\mu_1) + S_{di} S_{BDi} \text{ str. (B)}(\mu=\mu_1) = S_{di} \text{ str. (A, B)}(Di:\mu=\mu_1);$$

$$\Delta H = S_{di} Q_{Di} \quad (44)$$

$$(S_{pi} + S_{di} S_{Adi}) \text{ str. A}(\mu=\mu_1) + S_{di} S_{BDi} \text{ str. B}(\mu=\mu_1) = 1 \text{ str. (A, B)}(Fi:\mu=\mu_1);$$

$$\Delta H = Q_{Fi} = \left(\frac{\Delta H}{s}\right)_i + S_{di} Q_{Di} \quad (45)$$

If the i th mixing is one of a series, $Q_{Di} = Q_{F(i-1)}$ and the formula may be written

$$Q_{Fi} = \left(\frac{\Delta H}{s}\right)_i + S_{di} Q_{F(i-1)} \quad (46)$$

13. Definition. We define the apparent strionic heat content of the solute in a solution as

$$\Phi_s H = \frac{H - n_1 H_1}{s}, \quad (47)$$

where H equals the heat content of the solution, $n_1 H_1$ equals the heat content of the pure solvent contained in the solution, and s equals the number of strions of solute. Also, we define

$$\sigma = \frac{d \Phi_s H}{d \sqrt{u}}. \quad (48)$$

DISCUSSION OF ERRORS

Defects in the Apparatus

1. Dilution pipet.--The dilution pipet was carefully tested for leakage. The method used is described by Buck.¹³ The results showed that the pipet is leak-proof when properly sealed with vaseline.

It might be feared that an appreciable heat effect due to friction would accompany the opening of the pipet. In order that this error be estimated, several blank determinations were performed, in each of which the Dewar and the pipet contained the same solution. In each of these experiments, the heat of opening was found to be negligible.

¹³Loc. cit.

2. Calorimeter.--The design of the calorimeter was such that the chance of water from the bath leaking into the calorimeter was greatly reduced since the cemented joint was not exposed to the bath and since an effective gasket was used. As leakage of this type might ruin an entire series of experiments, the calorimeter was carefully examined after each experiment. No evidence of leakage was observed.

3. Standard resistances.--At the beginning of the work, the three standard resistances were compared with one another by means of a calibrated type-K potentiometer. The ratios found agreed excellently with the corresponding ratios of the nominal values.

4. Standard cell.--The Eppley standard cell was compared on the type-K potentiometer with each of three other standard cells. The EMF values which had been used for these cells were found to agree with the relative values obtained in this comparison within 0.01%.

Defects in the Materials

1. Errors in the composition of solutions.--The effect (upon Q_F) of errors in the composition of solutions may be resolved into two component effects: first, the effect of a discrepancy between the ionic strengths of the two solutions being mixed; and second, the effect of the deviation of the actual ionic strength from the ionic strength at which the mixing is assumed to take place.

To examine the first effect, let us consider a mixing experiment in which the ionic strengths are not quite the same. Suppose that the discrepancy between the ionic strengths of two solutions, one containing solute A and one solute B, is x ; and suppose that the heat of mixing is Q_F . We write the following equations:

$$S_A \text{ str. } A(\mu=\mu_1-x) + S_B \text{ str. } B(\mu=\mu_1) = 1 \text{ str. } (A,B)(\mu=\mu_1 \frac{\mu_1-x}{\mu_1-S_B x});$$

$$\Delta H = Q_F. \quad (49)$$

$$S_A \text{ str. } A(\mu=\mu_1 \frac{\mu_1-x}{\mu_1-S_B x}) = S_A \text{ str. } A(\mu=\mu_1-x);$$

$$\Delta H = C_A. \quad (50)$$

$$S_B \text{ str. } B(\mu=\mu_1 \frac{\mu_1-x}{\mu_1-S_B x}) = S_B \text{ str. } B(\mu=\mu_1); \quad \Delta H = C_B. \quad (51)$$

$$S_A \text{ str. } A(\mu=\mu_1 \frac{\mu_1-x}{\mu_1-S_B x}) + S_B \text{ str. } B(\mu=\mu_1 \frac{\mu_1-x}{\mu_1-S_B x}) = 1 \text{ str. } (A, B)(\mu=\mu_1 \frac{\mu_1-x}{\mu_1-S_B x});$$

$$\Delta H = Q_F(\text{Corr.}) = Q_F + C_A + C_B. \quad (52)$$

That is, the heat of mixing at equal ionic strengths can be calculated from the heat of mixing at unequal ionic strengths by correcting for the heat of dilution (or concentration) of each solute. The corrections C_A and C_B are obtainable from the σ -plots (see "Definitions and Propositions," no. 13) for the two solutes as follows:

$$\sigma = \frac{d \Phi_s H}{d \sqrt{u}} \approx \frac{\Delta \Phi_s H}{\Delta \sqrt{u}} \quad (53)$$

$$\Delta H = s \Delta \Phi_s H = s \cdot \sigma \Delta \sqrt{u} = \frac{1}{2} s \cdot \sigma \frac{\Delta \mu}{\sqrt{\mu}} \quad (54)$$

$$C_A = \frac{1}{2} \frac{S_A \sigma_A}{\sqrt{\mu_1}} \left[\mu_1^{-x} - \left(\mu_1 \frac{\mu_1-x}{\mu_1-S_B x} \right) \right] = - \frac{1}{2} \frac{S_A S_B x}{\sqrt{\mu_1}} \cdot \sigma_A \quad (55)$$

$$C_B = \frac{1}{2} \frac{S_B \sigma_B}{\sqrt{\mu_1}} \left[\mu_1 - \left(\mu_1 \frac{\mu_1-x}{\mu_1-S_B x} \right) \right] = \frac{1}{2} \frac{S_A S_B x}{\sqrt{\mu_1}} \cdot \sigma_B \quad (56)$$

The total correction is

$$C = C_A + C_B = \frac{1}{2} S_A S_B \sqrt{\mu_1} \left(\frac{x}{\mu_1} \right) (\sigma_B - \sigma_A). \quad (57)$$

Its value depends on the strion fraction, the ionic strength, the relative discrepancy in the ionic strengths, and the difference in σ for the two solutes at the ionic strength μ_1 .

For all the experiments in which the two solutes sodium chloride and sodium sulfate were mixed, a constant relative discrepancy in the ionic strengths of 0.0007 occurred (see "Preparation and Analysis of Solutions," par. 2). In order that the effect on the results be estimated, it was necessary that σ -plots be constructed for the two solutes. Sufficient data for NaCl and data for Na_2SO_4 in the dilute region were already available.¹⁴ To complete the plot for Na_2SO_4 , eight short-chord dilu-

¹⁴(a) Young and Machin, *J. Am. Chem. Soc.*, **58**, 2254 (1936);
(b) Young and Seligmann, *J. Am. Chem. Soc.*, **60**, 2379 (1938).

lutions were made. The results are shown in Table IV. In Fig. 5 are shown the σ -plots for the two solutes. Values of the correction C for NaCl and Na_2SO_4 at the ionic strengths actually used are shown below. These values were calculated for an assumed relative ionic strength discrepancy of 0.001 and a strion fraction of one-half.

$$\text{For } S_{\text{Na}_2\text{SO}_4} = \frac{1}{2}; \quad \frac{x}{\mu} = 0.001$$

μ	σ_{NaCl}	$\sigma_{\text{Na}_2\text{SO}_4}$	$\sigma_{\text{Na}_2\text{SO}_4} - \sigma_{\text{NaCl}}$	C (15° cal.)
0.2	- 31.	- 25.0	6.0	0.00
0.5	-200.	-162.5	37.5	0.00
1.0	-331.	-271.0	60.0	0.01
2.0	-393.	-337.5	55.5	0.01
5.0	-193.	-303.0	-110.0	-0.03

The results show that the error produced in Q for NaCl and Na_2SO_4 by a relative ionic strength discrepancy of 0.001 is negligible except at an ionic strength of 5, where it is harmlessly small.

All the experiments except the NaCl- Na_2SO_4 experiments were performed at unit ionic strength; hence the calculation of the error produced in Q for one of these experiments by a given relative ionic strength discrepancy requires only a knowledge of the difference in the values of σ for the two solutes at $\mu = 1$ (see eq. (57)). For most of the solute pairs investigated, the difference $\sigma_B - \sigma_A$ is less numerically than 200; for each of these solute-pairs, the error produced in Q at a strion fraction of one-half by a relative ionic strength discrepancy of 0.001 is less than 0.025 cal. For each of the few solute pairs for which $\sigma_B - \sigma_A$ is greater than 200, the heat of mixing is large, so that the per cent error in Q is small. For example, $\sigma_B - \sigma_A$ has a larger value (780) for the pair NaCl, HCl than for any other solute-pair; yet, the error produced in Q by a relative ionic strength discrepancy of 0.001 is only 0.10 cal., or only 0.3 per cent. Hence, barring the occurrence of unusual mistakes in the analysis of solutions, errors resulting from differences in ionic strength are unimportant.

In order to examine the second effect, one must possess data for experiments carried out at some constant strion fraction and at various ionic strengths, the same two solutes being used throughout. If we represent by $(\frac{\partial Q_F}{\partial \mu})_{S_F}$ the rate of change of Q_F with μ at constant strion fraction, then the error in Q_F corresponding to a relative error $\frac{\Delta \mu}{\mu}$ in μ is given by

$$\Delta Q_F = \mu \left(\frac{\partial Q_F}{\partial \mu} \right)_{S_F} \cdot \left(\frac{\Delta \mu}{\mu} \right). \quad (58)$$

In the case of the $\text{NaCl-Na}_2\text{SO}_4$ mixings, the necessary data were available. For each of several strion fractions, the derivative was obtained from the $Q_F\text{-}\mu$ data by means of a "chord-area" plot. The error ΔQ_F , corresponding to an assumed relative error of 0.005 in μ , was then calculated for each of the five ionic strengths at which experiments were performed. The results for the case in which the strion fraction of Na_2SO_4 is one-half are as follows:

$$S_{\text{Na}_2\text{SO}_4}(F) = \frac{1}{2}; \quad \frac{\Delta \mu}{\mu} = 0.005$$

μ	$\left(\frac{\partial Q_F}{\partial \mu} \right)_{S_F}$	ΔQ_F
0.2	-8.6	-0.01
0.5	-5.9	-0.01
1.0	-3.9	-0.02
2.0	-1.6	-0.02
5.0	-0.1	-0.00

The results are similar for the other strion fractions for which the calculations were made. Since the relative error assumed was much larger than one would expect, it follows that errors from this source are negligible.

2. Errors due to impurities.--The heat effect caused by the presence of traces of impurities that did not "react" during the mixing would be very small indeed; for one of the conclusions drawn in this paper is that the heat of mixing at constant ionic strength is small, and therefore the replacement of a small amount of solute by a small amount of another solute (the impurity) would have a negligible effect on the heat of mixing. If, on the other hand, the impurity could undergo a chemical change during the mix-

ing, an appreciable heat effect might result. Thus, consider the mixing of NaCl in the Dewar and HCl in the pipet at unit ionic strength, the total volume of solution being 750 cc. The concentration of hydrogen ion after mixing would be $[H^+] = 0.1$. Suppose the NaCl contained 0.01% SO_4 . Then the total sulfate concentration after mixing would be $[SO_4^{=}] + [HSO_4^-] = 5.5 \times 10^{-5}$. The dissociation constant of HSO_4^- is 0.010 at 25° . Its heat of formation from its ions is 5000 cal./mol.

$$\frac{[H^+][SO_4^{=}]}{[HSO_4^-]} = \frac{0.1[SO_4^{=}]}{[HSO_4^-]} = 0.010$$

$$[HSO_4^-] = 5 \times 10^{-5}$$

The amount of HSO_4^- formed would be $0.75 \times 5 \times 10^{-5}$ moles and the formation of this much HSO_4^- would liberate $4 \times 10^{-5} \times 5000$ cal. = 0.2 cal., an error which is appreciable but not serious. Actually, the NaCl contained not greater than 0.001% SO_4 (according to the label on the bottle), so the error was trivial. Similarly, small heat effects might arise in the mixing of HCl with a salt due to the union of H^+ ion and HCO_3^- ion, the latter being due either to the presence of carbonates in the salt or to CO_2 from the air. Certainly, the presence of impurities caused little error in the mixings involving salts alone.

Another possible source of error lies in the contamination of solutions while they are in the calorimeter. Ralston¹⁵ has shown that the vaseline used is practically free of electrolytes. In general, the results show, because of their consistency, that this source of error is unimportant.

Defects in Procedure

1. Lack of thermal equilibrium.--If the calorimeter were not in thermal equilibrium with the bath before the opening of the pipet, so that the temperature inside the Dewar were drifting considerably, then the temperature inside the pipet would lag behind that in the Dewar; and, as a result, the opening of the pipet would be accompanied by a spurious heat effect. To insure thermal equilibrium and thus eliminate this error, the pipet was not opened until the thermal EMF had been drifting at not greater than 0.02 microvolt per minute for an hour or more.

¹⁵Ralston, Ph. D. Dissertation, University of Chicago, 1940.

2. Correction of $\Delta H/s$ from t° to 25° .--For the purpose of estimating the rate of change of the heat of mixing with temperature, a knowledge of which is necessary for the conversion of values of $\frac{\Delta H}{s}$ (at the temperatures at which the experiments were performed) to values of $\frac{\Delta H}{s}$ at 25.00° , several experiments in the mixing of NaCl and Na_2SO_4 were performed at 20° and several at 23° (the experiments at the ionic strength $\mu = 5$ were carried out at 23° instead of at 20° since sodium sulfate is not sufficiently soluble at 20°). The results are given in Table V. The experiments at 20° and those at 23° were duplicates, except for temperature, of experiments carried out at 25° (see Tables I,C; I,D; and I,E). For each pair of experiments, the values of Q_F at the two temperatures were converted to values at round strion fractions by extrapolation and interpolation. The quantity $\frac{1}{Q_F(25^\circ)} \cdot \frac{\Delta Q_F}{\Delta t}$ was then computed. The results for the different ionic strengths are as follows:

$$\mu = 1$$

$S_{\text{Na}_2\text{SO}_4}$	$Q_F(25.01^\circ)$	$Q_F(20.10^\circ)$	$\frac{1}{Q_F(25^\circ)} \cdot \frac{\Delta Q_F}{\Delta t}$
.1000	-2.23	-2.70	-0.043

$$\mu = 2$$

$S_{\text{Na}_2\text{SO}_4}$	$Q_F(25.10^\circ)$	$Q_F(20.12^\circ)$	$\frac{1}{Q_F(25^\circ)} \cdot \frac{\Delta Q_F}{\Delta t}$
.1000	-2.71	-3.34	-0.047
.2000	-5.08	-6.26	-0.047

$$\mu = 5$$

$S_{\text{Na}_2\text{SO}_4}$	$Q_F(25.14^\circ)$	$Q_F(23.04^\circ)$	$\frac{1}{Q_F(25^\circ)} \cdot \frac{\Delta Q_F}{\Delta t}$
.1000	-2.31	-2.37	-0.012
.2000	-4.75	-4.87	-0.012

The results are summarized as follows, the symbol α representing the quantity $\frac{1}{Q_F(25.0^\circ)} \cdot \frac{\Delta Q_F}{\Delta t}$

μ	α
1.	-0.043
2.	-0.047
5.	-0.012

The correction to be added for the conversion of $Q_F(t^\circ)$ to $Q_F(25.00^\circ)$ is given by the expression

$$\Delta Q_F = \alpha Q_F(25.00^\circ - t^\circ), \quad (59)$$

which is valid only if all the experiments of the series contributing to the value of Q_F were performed at exactly the same temperature. It is easily shown that the correction for $\frac{\Delta H}{s}$ (and there is no restriction here) is given by the expression

$$C = \alpha \frac{\Delta H}{s} (25.00^\circ - t^\circ). \quad (60)$$

The corrections for $\frac{\Delta H}{s}$ were computed and applied for all the experiments in which sodium chloride and sodium sulfate were mixed, α being taken as -0.04 at $\mu = 0.2$ and at $\mu = 0.5$. The corrections were negligible at ionic strengths of 0.2, 0.5, and 1 and their application produced no changes in the values of $\frac{\Delta H}{s}$, the latter being expressed to two decimal places. At ionic strengths of 2 and 5, however, slight changes in $\frac{\Delta H}{s}$ were produced, as can be observed in Tables I, D and I, E. Experiments in which sodium chloride and potassium chloride were mixed, and experiments in which sodium chloride and lithium chloride were mixed, were all performed at 25.00° , and no temperature corrections were necessary. For all other mixing experiments at 25° , temperature corrections were not computed; but the temperatures of these experiments differed only slightly from 25.00° , and the corrections were surely negligible.

3. Calculation of heater resistance.--A small error was incurred in the calculation of the resistance of the heater because the simplified approximate formula $R = 1000.0 \frac{P}{Q}$ was used instead of the exact expression

$$R = 1000.1 \frac{P}{Q} - 0.3, \quad (61)$$

which corrects for the resistance of the leads. Since the ratio

$\frac{P}{Q}$ has a value near unity, the correct expression is practically equivalent to

$$R = 1000.0 \frac{P}{Q} - 0.2. \quad (62)$$

The error caused by the use of the approximate formula is, therefore, $\frac{0.2}{R}(100\%) = 0.02\%$, which is trivial.

RESULTS

The experiments performed are classified and summarized as follows, references being given to tables and figures.

- I. Complete Series of Mixing Experiments at 25° Covering the Entire Range of Strion Fraction and Ionic Strength: NaCl and Na_2SO_4 .
 - A. $\mu = 0.2$ Table I,A; Fig. 1(a)
 - B. $\mu = 0.5$ Table I,B; Fig. 1(b)
 - C. $\mu = 1.$ Table I,C; Fig. 1(c)
 - D. $\mu = 2.$ Table I,D; Fig. 1(d)
 - E. $\mu = 5.$ Table I,E; Fig. 1(e)
- II. Complete Series of Mixing Experiments at 25° and at Unit Ionic Strength, Covering the Entire Range of Strion Fraction.
 - A. NaCl and KCl Table II,A; Fig. 3
 - B. NaCl and LiCl Table II,B; Fig. 4
- III. Short Sets of Mixing Experiments at 25° and at Unit Ionic Strength, Only Partially Covering the Strion Fraction Range.
 - A. NaCl and HCl Table III,A
 - B. KCl and LiCl Table III,B
 - C. KCl and Na_2SO_4 Table III,C
 - D. NaCl and NaBr Table III,D
 - E. NaCl and NaNO_3 Table III,E
 - F. KCl and NaNO_3 Table III,F
 - G. NaCl and KNO_3 Table III,G
 - H. KCl and NaBr Table III,H
- IV. Experiments at 25° in the Heat of Dilution of Sodium Sulfate.
 - Table IV; Fig. 5
- V. Short Sets of Mixing Experiments at Temperatures Other than 25° : NaCl and Na_2SO_4 .
 - A. $\mu = 1., t = 20^\circ$ Table V,A
 - B. $\mu = 2., t = 20^\circ$ Table V,B
 - C. $\mu = 5., t = 23^\circ$ Table V,C

The first column in each of Tables I,D and I,E contains the ordinal number of each experiment in that table. The second column gives the strion fraction of one solute in the final solution after mixing. The third column gives the Centigrade temperature at which the mixing took place. In the fourth column is found the ΔH of mixing (in 15° calories) per strion of solute. The fifth column contains ΔH per strion corrected to 25.00° (see "Discussion of Errors," sec. C, no. 2). The sixth column also contains the value of ΔH per strion at 25.00° , corrected in a manner to be described in the next paragraph. In the seventh column is the strion fraction of solute contained in the Dewar before mixing. The eighth column gives (also in 15° calories) the value of Q at 25.00° (see "Definitions and Propositions," no. 9) for the final solution after mixing, calculated by means of equation (46). For all tables other than Tables I,D and I,E, $(\frac{\Delta H}{s})_{25.00^\circ}$ is equal to $(\frac{\Delta H}{s})_t$ for each experiment, and one column contains both quantities.

The values of $(\frac{\Delta H}{s})_{25.00^\circ}$ in a given series were smoothed in the following manner. Denote by A the solute whose solution was placed in the pipet and mixed in the Dewar with solutions containing both A and B. Denote by ΔS_B the difference $S_{BF} - S_{BD}$, and by S_B (Mean) the quantity $\frac{1}{2} (S_{BF} + S_{BD})$. In this nomenclature, the procedure followed was to plot the quotient $\frac{\Delta H/s}{\Delta S_B}$ against S_B (Mean) for all the experiments of the series. The "best smooth curve" was then drawn for these points, and "smoothed" values of $\frac{\Delta H/s}{\Delta S_B}$ were read from the curve at the abscissas of these points. The "smoothed" values of $\frac{\Delta H}{s}$ were obtained when each "smoothed" $\frac{\Delta H/s}{\Delta S_B}$ was multiplied by the corresponding ΔS_B . The precision of the measurements is reflected in the close agreement, except in occasional instances, between the experimental $\Delta H/s$ and the "smoothed" $\Delta H/s$. The apparently large discrepancies between these quantities for a few of the experiments listed in Table I,A result from the fact that the heat effects observed at an ionic strength of 0.2 are very small and hence the per cent error is large. It is interesting to note that the curves $\frac{\Delta H/s}{\Delta S_B}$ vs. S_B (Mean) flatten out as the ionic strength decreases, becoming nearly linear at $\mu = 0.2$. It is easily demonstrated on theoretical grounds that these curves must pass through the origin; that is,

$$S_B(\text{Mean}) \xrightarrow{L} 0 \quad \frac{\Delta H/s}{\Delta S_B} = 0.$$

For the experiments of Table III and those of Table V, the values of $\Delta H/s$ were not smoothed since the series were too short to permit the drawing of the requisite curves.

In Table IV, the quantity $\Delta \Phi_s H$ in the sixth column is the ΔH of dilution per strion of solute. In the seventh column, the $\frac{\Delta \Phi_s H}{\Delta \sqrt{u}}$, where $\Delta \sqrt{u} = \sqrt{u_2} - \sqrt{u_1}$, is the average value of σ (see "Definitions and Propositions," no. 13) for the concentration range $\sqrt{u_2} - \sqrt{u_1}$.

TABLE I, A -- NaCl, Na₂SO₄; $\mu = 0.2$

No.	S _{Na₂SO₄} (F)	t° ± .01°	($\frac{\Delta H}{s}$) _{t°} = ($\frac{\Delta H}{s}$) _{25°}	($\frac{\Delta H}{s}$) _{25°} , "Smoothed"	S _d	Q _F (25°), 15° cal.
1	.10077	24.98	-0.72	-0.78	.89923	-0.78
2	.19031	25.00	-0.77	-0.62	.90042	-1.32
3	.27096	25.01	-0.47	-0.50	.90041	-1.69
4	.34393	25.01	-0.43	-0.41	.89990	-1.93
5	.40934	25.03	-0.36	-0.33	.90030	-2.07
6	.89922	25.00	-0.73	-0.78	.89922	-0.78
7	.80882	25.00	-0.65	-0.63	.89946	-1.33
8	.72844	25.00	-0.50	-0.50	.90063	-1.70
9	.65605	25.00	-0.43	-0.41	.90062	-1.94
10	.58986	25.00	-0.35	-0.33	.89910	-2.07
11	.09921	25.00	-0.75	-0.76	.90079	-0.76
12	.18994	25.00	-0.63	-0.63	.89928	-1.31
13	.90097	25.00	-0.69	-0.76	.90097	-0.76

TABLE I, B -- NaCl, Na₂SO₄; $\mu = 0.5$

No.	S _{Na₂SO₄} (F)	t° ± .01°	($\frac{\Delta H}{s}$) _{t°} = ($\frac{\Delta H}{s}$) _{25°}	($\frac{\Delta H}{s}$) _{25°} , "Smoothed"	S _d	Q _F (25°), 15° cal.
1	.10020	25.00	-1.46	-1.51	.89980	-1.51
2	.18912	25.00	-1.23	-1.21	.90118	-2.57
3	.27084	25.00	-1.02	-1.00	.89922	-3.31
4	.34505	25.00	-0.80	-0.82	.89822	-3.79
5	.41172	25.00	-0.63	-0.66	.89820	-4.06
6	.47094	24.99	-0.55	-0.53	.89934	-4.18
7	.90000	25.06	-1.48	-1.51	.90000	-1.51
8	.80774	25.06	-1.24	-1.25	.89749	-2.61
9	.72384	25.07	-1.04	-1.02	.89613	-3.36
10	.65062	25.00	-0.82	-0.80	.89884	-3.82
11	.58498	25.00	-0.66	-0.64	.89912	-4.07
12	.52687	25.00	-0.53	-0.51	.90066	-4.18
13	.90909	25.06	-1.39	-1.38	.90909	-1.38

TABLE I, C -- NaCl, Na₂SO₄; $\mu = 1$

No.	S _{Na₂SO₄} (F)	t° ± .01°	($\frac{\Delta H}{s}$) _{t°} = ($\frac{\Delta H}{s}$) _{25°}	($\frac{\Delta H}{s}$) _{25°} , "Smoothed"	S _d	Q _F (25°), 15° cal.
1	.10498	25.01	-2.34	-2.34	.89502	-2.34
2	.19711	25.01	-1.90	-1.90	.89706	-4.00
3	.28082	25.00	-1.62	-1.60	.89574	-5.18
4	.35490	25.02	-1.31	-1.32	.89700	-5.97
5	.42114	25.01	-1.10	-1.10	.89732	-6.45
6	.47981	25.02	-0.92	-0.92	.89864	-6.72
7	.90041	25.01	-2.63	-2.63	.90041	-2.63
8	.81109	25.01	-2.05	-2.05	.90080	-4.42
9	.73121	25.00	-1.60	-1.60	.90152	-5.58
10	.65884	25.01	-1.32	-1.27	.90102	-6.30
11	.59349	25.01	-1.01	-1.01	.90081	-6.69
12	.53479	25.01	-0.81	-0.80	.90109	-6.83

TABLE I,D -- NaCl, Na₂SO₄; $\mu = 2$

No.	S _{Na₂SO₄} (F)	t° ± .01°	($\frac{\Delta H}{s}$) _{t°}	($\frac{\Delta H}{s}$) _{25°}	($\frac{\Delta H}{s}$) _{25°} , "Smoothed"	S _d	Q _F (25°), 15° cal.
1	.10509	25.09	-2.85	-2.86	-2.86	.89491	-2.86
2	.20049	25.10	-2.55	-2.56	-2.56	.89340	-5.11
3	.28658	25.09	-2.22	-2.23	-2.24	.89232	-6.80
4	.36182	25.09	-1.87	-1.88	-1.87	.89454	-7.95
5	.42898	25.09	-1.58	-1.58	-1.59	.89476	-8.70
6	.48816	25.09	-1.32	-1.33	-1.32	.89637	-9.12
7	.90165	25.07	-3.90	-3.92	-3.91	.90165	-3.91
8	.81124	25.06	-2.98	-2.99	-2.99	.89972	-6.51
9	.73025	25.08	-2.22	-2.23	-2.23	.90017	-8.08
10	.65663	25.09	-1.68	-1.69	-1.69	.89918	-8.96
11	.59061	25.09	-1.30	-1.30	-1.27	.89945	-9.32
12	.53076	25.09	-0.97	-0.97	-0.97	.89867	-9.35
13	.89971	25.09	-3.97	-3.98	-3.99	.89971	-3.99
14	.80818	25.09	-3.00	-3.01	-3.01	.89826	-6.59

TABLE I,E -- NaCl, Na₂SO₄; $\mu = 5$

No.	S _{Na₂SO₄} (F)	t° ± .01°	($\frac{\Delta H}{s}$) _{t°}	($\frac{\Delta H}{s}$) _{25°}	($\frac{\Delta H}{s}$) _{25°} , "Smoothed"	S _d	Q _F (25°), 15° cal.
1	.10821	25.14	-2.51	-2.51	-2.51	.89179	-2.51
2	.20495	25.13	-2.63	-2.64	-2.64	.89153	-4.87
3	.29118	25.13	-2.58	-2.58	-2.59	.89153	-6.93
4	.36750	25.13	-2.42	-2.42	-2.42	.89233	-8.61
5	.43503	25.04	-2.20	-2.20	-2.20	.89324	-9.88
6	.49535	25.05	-1.97	-1.97	-1.98	.89324	-10.81
7	.90114	25.12	-5.93	-5.94	-5.94	.90114	- 5.94
8	.81078	25.13	-4.02	-4.03	-4.03	.89972	- 9.37
9	.72958	25.13	-2.66	-2.67	-2.67	.89985	-11.10
10	.65589	25.13	-1.78	-1.78	-1.78	.89899	-11.75
11	.58976	25.14	-1.15	-1.16	-1.16	.89919	-11.73
12	.52952	25.14	-0.77	-0.77	-0.76	.89785	-11.29

TABLE II,A -- NaCl, KCl; $\mu = 1$

No.	$S_{\text{KCl(F)}}$	$t^{\circ} \pm .01^{\circ}$	$(\frac{\Delta H}{s})_{t^{\circ}} = (\frac{\Delta H}{s})_{25^{\circ}}$	$(\frac{\Delta H}{s})_{25^{\circ}}$, "Smoothed"	S_d	$Q_F(25^{\circ})$, 15°cal.
1	.09740	25.00	-3.32	-3.32	.90260	-3.32
2	.18735	25.00	-2.78	-2.78	.90034	-5.76
3	.26830	25.00	-2.24	-2.26	.90040	-7.45
4	.34119	25.00	-1.85	-1.85	.90038	-8.56
5	.40597	25.00	-1.50	-1.50	.90168	-9.22
6	.46481	25.00	-1.26	-1.26	.90095	-9.56
7	.89939	25.00	-3.46	-3.46	.89939	-3.46
8	.80888	25.00	-2.83	-2.83	.89937	-5.94
9	.72769	25.00	-2.29	-2.29	.89962	-7.63
10	.65431	25.00	-1.86	-1.86	.89917	-8.72
11	.58836	25.00	-1.49	-1.49	.89921	-9.33
12	.52994	25.00	-1.17	-1.17	.90070	-9.58

TABLE II,B -- NaCl, LiCl; $\mu = 1$

No.	$S_{\text{LiCl(F)}}$	$t^{\circ} \pm .01^{\circ}$	$(\frac{\Delta H}{s})_{t^{\circ}} = (\frac{\Delta H}{s})_{25^{\circ}}$	$(\frac{\Delta H}{s})_{25^{\circ}}$, "Smoothed"	S_d	$Q_F(25^{\circ})$, 15°cal.
1	.09957	25.00	7.14	7.14	.90043	7.14
2	.18903	25.00	5.95	5.95	.90065	12.38
3	.26953	25.00	4.94	4.94	.90075	16.09
4	.34203	25.00	4.10	4.09	.90074	18.58
5	.40792	25.00	3.39	3.41	.89986	20.13
6	.46712	25.00	2.81	2.81	.90002	20.92
7	.89998	25.00	8.14	8.14	.89998	8.14
8	.81087	25.00	6.29	6.31	.90099	13.64
9	.73067	25.00	4.98	4.98	.90109	17.27
10	.65849	25.00	3.94	3.93	.90121	19.50
11	.59223	25.00	3.14	3.15	.89938	20.69
12	.53258	25.00	2.49	2.49	.89928	21.10

TABLE III,A -- NaCl, HCl; $\mu = 1$

No.	$S_{\text{HCl(F)}}$	$t^\circ \pm .01^\circ$	$(\frac{\Delta H}{s})_{t^\circ} = (\frac{\Delta H}{s})_{25^\circ}$	S_d	$Q_F(25^\circ),$ 15° cal.
1	.09996	25.00	10.68	.90004	10.68
2	.18918	25.00	9.11	.90087	18.73
3	.89959	24.99	12.74	.89959	12.74
4	.80960	24.98	9.82	.89997	21.29

TABLE III,B -- KCl, LiCl; $\mu = 1$

No.	$S_{\text{KCl(F)}}$	$t^\circ \pm .01^\circ$	$(\frac{\Delta H}{s})_{t^\circ} = (\frac{\Delta H}{s})_{25^\circ}$	S_d	$Q_F(25^\circ),$ 15° cal.
1	.09921	24.98	- 5.94	.90079	- 5.94
2	.18934	25.01	- 4.80	.89995	-10.14
3	.89819	25.00	- 5.65	.89819	- 5.65
4	.80692	24.99	- 4.65	.89839	- 9.72

TABLE III,C -- KCl, Na_2SO_4 ; $\mu = 1$

No.	$S_{\text{KCl(F)}}$	$t^\circ \pm .01^\circ$	$(\frac{\Delta H}{s})_{t^\circ} = (\frac{\Delta H}{s})_{25^\circ}$	S_d	$Q_F(25^\circ),$ 15° cal.
1	.09819	24.99	-0.35	.90181	-0.35
2	.89785	24.99	0.67	.89785	0.67

TABLE III,D -- NaCl, NaBr; $\mu = 1$

No.	$S_{\text{NaBr(F)}}$	$t^\circ \pm .01^\circ$	$(\frac{\Delta H}{s})_{t^\circ} = (\frac{\Delta H}{s})_{25^\circ}$	S_d	$Q_F(25^\circ),$ 15° cal.
1	.09921	25.01	0.28	.90079	0.28
2	.89988	25.00	0.29	.89988	0.29

TABLE III,E -- NaCl, NaNO₃; $\mu = 1$

No.	$S_{\text{NaNO}_3}(\text{F})$	$t^\circ \pm .01^\circ$	$(\frac{\Delta H}{s})_{t^\circ} = (\frac{\Delta H}{s})_{25^\circ}$	S_d	$Q_F(25^\circ),$ 15° cal.
1	.09938	25.00	1.21	.90062	1.21
2	.89935	25.00	1.02	.89935	1.02

TABLE III,F -- KCl, NaNO₃; $\mu = 1$

No.	$S_{\text{NaNO}_3}(\text{F})$	$t^\circ \pm .01^\circ$	$(\frac{\Delta H}{s})_{t^\circ} = (\frac{\Delta H}{s})_{25^\circ}$	S_d	$Q_F(25^\circ),$ 15° cal.
1	.09943	25.00	-35.52	.90057	-35.52
2	.89068	25.00	-36.21	.90068	-36.21

TABLE III,G -- NaCl, KNO₃; $\mu = 1$

No.	$S_{\text{KNO}_3}(\text{F})$	$t^\circ \pm .01^\circ$	$(\frac{\Delta H}{s})_{t^\circ} = (\frac{\Delta H}{s})_{25^\circ}$	S_d	$Q_F(25^\circ),$ 15° cal.
1	.09846	25.00	29.39	.90154	29.39
2	.89812	25.00	27.68	.89812	27.68

TABLE III,H -- KCl, NaBr; $\mu = 1$

No.	$S_{\text{NaBr}}(\text{F})$	$t^\circ \pm .01^\circ$	$(\frac{\Delta H}{s})_{t^\circ} = (\frac{\Delta H}{s})_{25^\circ}$	S_d	$Q_F(25^\circ),$ 15° cal.
1	.09815	25.01	- 6.68	.90185	- 6.68
2	.89880	25.01	- 6.75	.89880	- 6.75

TABLE IV -- DILUTION OF Na_2SO_4

No.	μ_1	$\sqrt{\mu_1}$	$\sqrt{\mu_2}$	$t^\circ \pm .01^\circ$	$\Delta\Phi_s H(t^\circ)$	$\frac{\bar{\sigma}(t^\circ) \Delta\Phi_s H}{\Delta\sqrt{\mu}}(t^\circ)$
1	.729755	.854257	.809815	24.99	9.535	-214.6
2	.809326	.899625	.854257	24.99	10.524	-232.0
3	1.63765	1.27971	1.21385	25.00	21.040	-319.5
4	1.82075	1.34935	1.27971	25.00	22.849	-328.1
5	3.06221	1.74992	1.65757	25.01	31.902	-345.4
6	3.41310	1.84746	1.74992	25.01	33.412	-342.6
7	5.13655	2.26640	2.14464	25.04	37.378	-307.0
8	5.73525	2.39484	2.26640	25.04	37.309	-290.5

TABLE V,A -- NaCl , Na_2SO_4 ; $\mu = 1$; $t = 20^\circ\text{C}$.

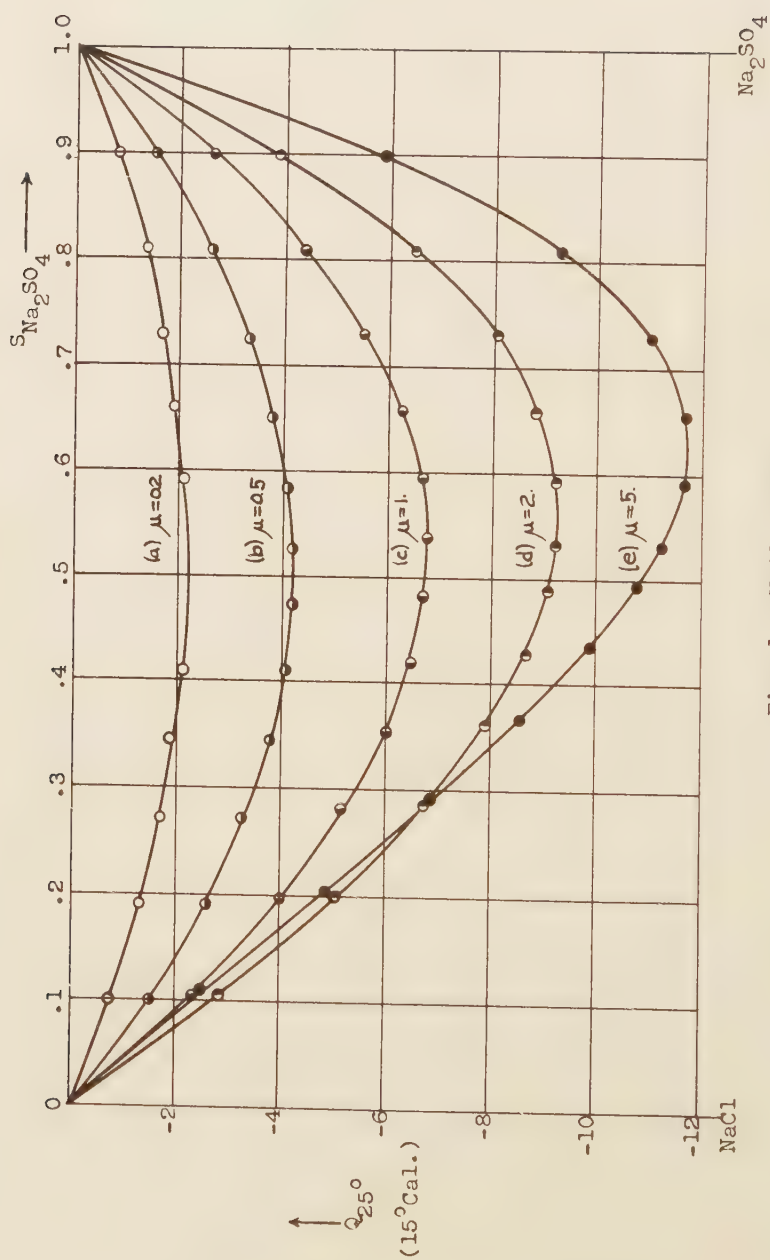
No.	$S_{\text{Na}_2\text{SO}_4}(\text{F})$	$t^\circ \pm .01^\circ$	$(\frac{\Delta H}{s})_{t^\circ}$	S_d	$Q_F(t^\circ), 15^\circ\text{cal.}$
1	.10040	20.10	-2.71	.89960	-2.71

TABLE V,B -- NaCl , Na_2SO_4 ; $\mu = 2$; $t = 20^\circ\text{C}$.

No.	$S_{\text{Na}_2\text{SO}_4}(\text{F})$	$t^\circ \pm .01^\circ$	$(\frac{\Delta H}{s})_{t^\circ}$	S_d	$Q_F(t^\circ), 15^\circ\text{cal.}$
1	.10170	20.12	-3.40	.89830	-3.40
2	.19225	20.12	-2.98	.89920	-6.04

TABLE V,C -- NaCl , Na_2SO_4 ; $\mu = 5$; $t = 23^\circ\text{C}$.

No.	$S_{\text{Na}_2\text{SO}_4}(\text{F})$	$t^\circ \pm .01^\circ$	$(\frac{\Delta H}{s})_{t^\circ}$	S_d	$Q_F(t^\circ), 15^\circ\text{cal.}$
1	.10527	23.04	-2.50	.89473	-2.50
2	.19842	23.04	-2.59	.89589	-4.83

Fig. 1.--NaCl, Na_2SO_4

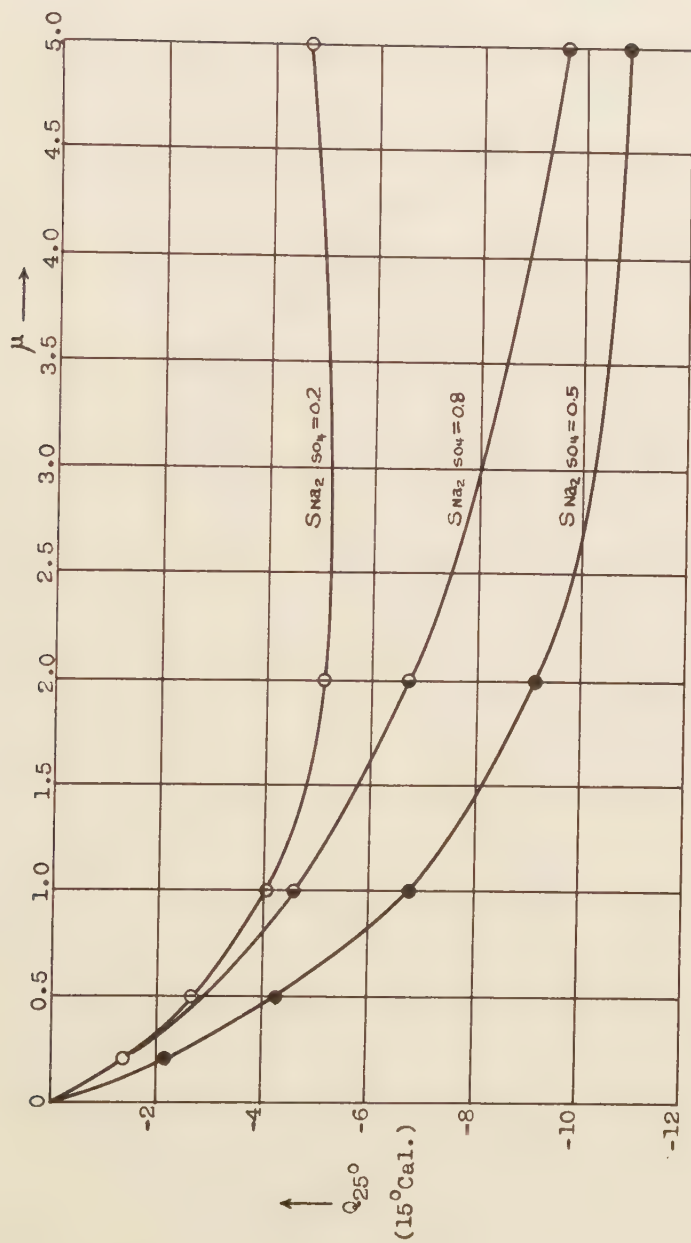


Fig. 2.--Constant-S Curves; NaCl, Na_2SO_4

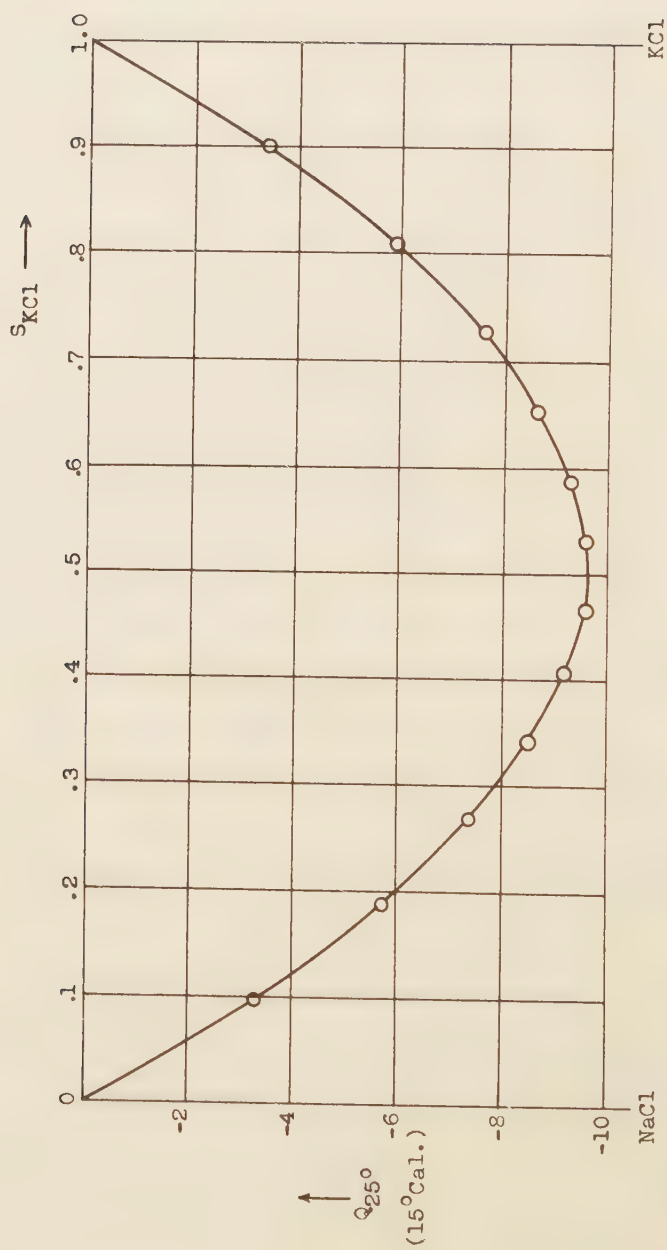


Fig. 3.-- $NaCl$, KCl ; $\mu = 1$

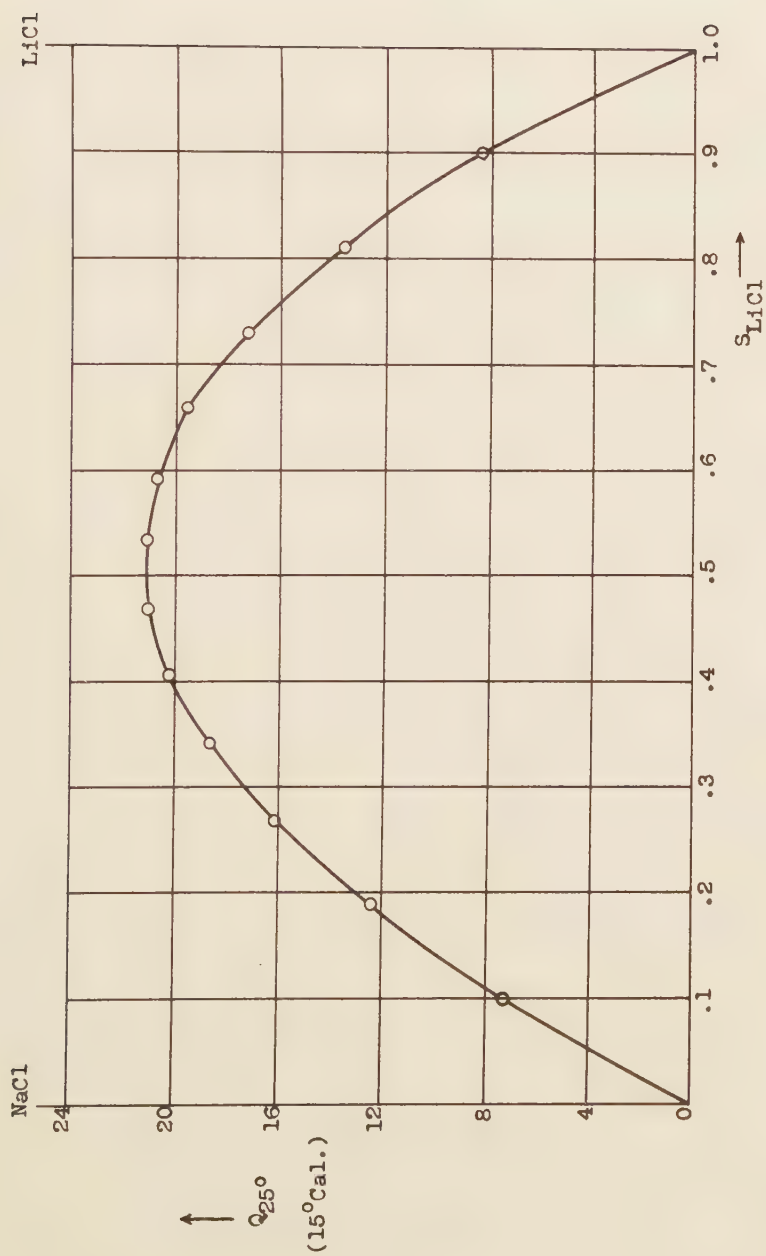


Fig. 4.--NaCl, LiCl; $\mu = 1$

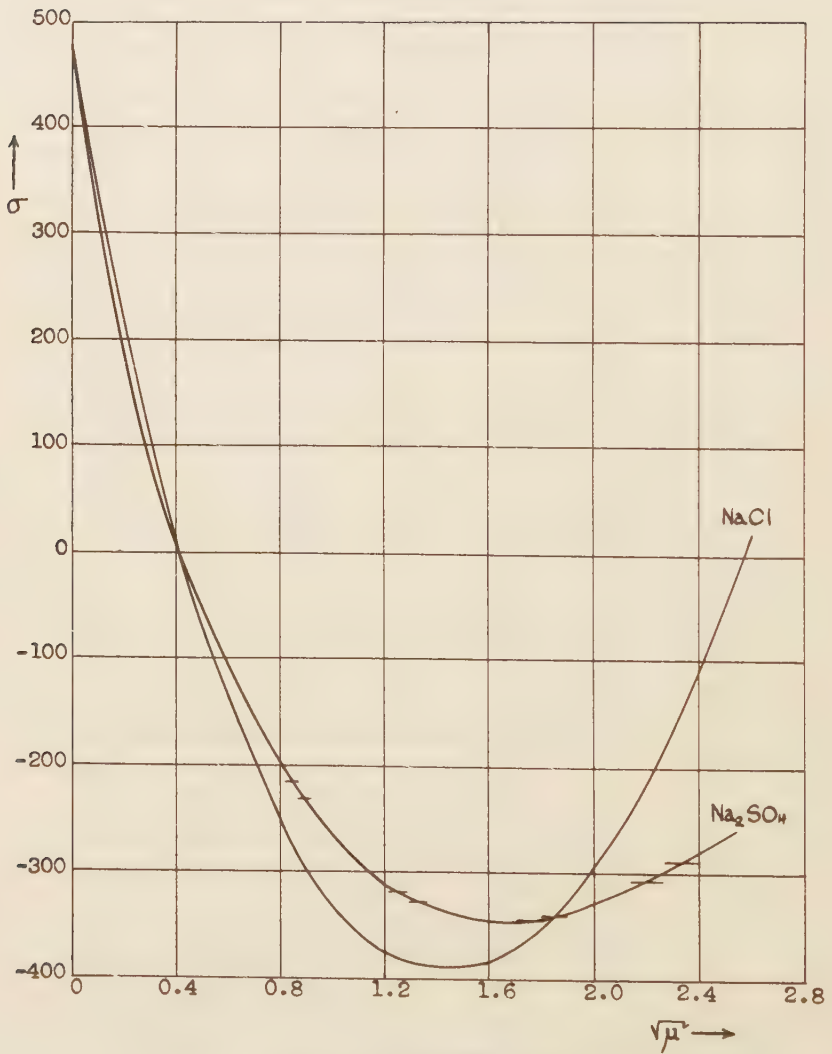


Fig. 5. -- $\sigma = \frac{d\phi_0 H}{d\sqrt{\mu}}$ vs $\sqrt{\mu}$

DISCUSSION OF THE RESULTS -- CONCLUSIONS

Discussion of the Curves

In Fig. 1, the data of Table I are plotted. The abscissa is the strion fraction of sodium sulfate and the ordinate is the heat of mixing per strion, Q_{250} , of the monosalt solutions of the same ionic strength. It is interesting to note that the five curves are much more closely bunched at the left end than at the right end, the curve for $\mu = 5$ crossing that for $\mu = 2$. In dilute solutions, the constant- μ curves are nearly symmetrical about the $S = 0.5$ axis and closely resemble segments of parabolas of the form

$$Q = -aS(1-S), \quad (63)$$

small values of the parameter a corresponding to small values of μ and to small values of Q . As the ionic strength is increased, however, the curves begin to show a lack of symmetry. At $\mu = 1$, the curve is distinctly unsymmetrical about the $S = 0.5$ axis, its minimum being displaced toward the right. The extent of the dissymmetry increases as the ionic strength is further increased; and, at $\mu = 5$, the minimum is displaced 0.125 strion fraction units to the right. Furthermore, the $\mu = 5$ curve exhibits a point of inflexion at $S_{\text{Na}_2\text{SO}_4} = 0.18$. The displacement of the minimum from $S = 0.5$ is given as a function of the ionic strength by the relation

$$D = S_{\text{Na}_2\text{SO}_4}(\text{Min.}) - 0.5 = \sqrt{0.0098(\mu + 1.80)} - 0.133. \quad (64)$$

In order to fit the curve for $\mu = 5$, an algebraic equation would have to be of degree not less than three. It was found that a cubic equation could not be made to fit the data well for either of the cases $\mu = 2$ or $\mu = 5$, but that each of the curves could be satisfactorily represented by a quartic equation. Although the curves for $\mu = 0.2$ and $\mu = 0.5$ should undoubtedly exhibit slight departures from symmetry, the data do not reveal them. These curves were therefore treated as symmetrical and quadratic equations were derived for them. The equations obtained for the five curves are as follows, $S_{\text{Na}_2\text{SO}_4}$ being abbreviated to S :

$$(a) \mu = 0.2 \quad Q = -8.55 S(1-S) \quad (65)$$

$$(b) \mu = 0.5 \quad Q = -16.78 S(1-S) \quad (66)$$

$$(c) \mu = 1. \quad Q = -24.00 S(1-S)(1 + 0.254 S) \quad (67)$$

$$(d) \mu = 2. \quad Q = -29.01 S(1-S)(1 + 0.445 S + 0.162 S^2) \quad (68)$$

$$(e) \mu = 5. \quad Q = -21.46 S(1-S)(1 + 1.804 S + 0.558 S^2) \quad (69)$$

In Fig. 2 are shown constant-S curves for the solute-pair NaCl, Na_2SO_4 , Q_{250} being plotted against μ . The values of Q_{250} for round values of $S_{\text{Na}_2\text{SO}_4}$ were obtained from the plots of Fig. 1. The curves appear to have finite limiting slopes. The limiting slope of the $S = 0.5$ curve was estimated to be -12, while that of the other 2 curves was estimated to be -7.4. In the dilute region ($\mu \leq 0.1$), then, the heats of mixing at the three strion fractions are given approximately by the relations:

$$\text{For } S_{\text{Na}_2\text{SO}_4} = 0.2 \text{ or } 0.8, \quad Q = -7.4 \mu \quad (70)$$

$$\text{For } S_{\text{Na}_2\text{SO}_4} = 0.5, \quad Q = -12 \mu \quad (71)$$

In Fig. 3, the data of Table II,A are represented in a constant- μ plot, the abscissa being the strion fraction of potassium chloride. The curve resembles in form the corresponding curve 1(c) for the solute-pair NaCl, Na_2SO_4 but is more symmetrical and lies below it, having an ordinate about 40% larger in absolute magnitude. The following cubic equation was found to fit the curve satisfactorily:

$$Q = -37.68 S(1-S)(1 + 0.030 S). \quad (72)$$

in which S represents S_{KCl} .

In Fig. 4, the constant- μ curve for the solute-pair NaCl, LiCl (see Table II,B) is plotted. This curve differs strikingly from preceding curves in that its ordinates are positive instead of negative (heat was absorbed instead of being evolved). If the curve were reflected through the $Q = 0$ axis, it would then resemble in form the corresponding curves for the other solute-pairs. Its ordinates, however, are three times as large in absolute magnitude as the corresponding ordinates ($\mu = 1$) for the solute-pair NaCl, Na_2SO_4 . The following hyperbolic equation was found to represent the curve satisfactorily:

$$Q = \frac{78.45 S(1-S)}{1-0.1443 S}, \quad (73)$$

where S represents S_{LiCl} .

In Fig. 5 are shown the σ -plot for NaCl and that for

Na_2SO_4 . Each short-chord of the Na_2SO_4 plot represents one of the heat of dilution experiments listed in Table IV. It is of interest to note the similarity in form of the two curves, not only in the dilute region, but also in the concentrated region. The limiting values of the two ordinates at infinite dilution are identical. This close resemblance emphasizes the advantage of plotting $\frac{d\phi_s H}{d\sqrt{\mu}}$ against $\sqrt{\mu}$ instead of plotting $\frac{d\phi H}{d\sqrt{m}}$ against $\sqrt{m}$. (When plotted in the latter manner, the curves for NaCl and Na_2SO_4 are widely different.)

Magnitude of the Heat of Mixing at Equal Ionic Strengths

In the appraisal of the magnitude of the heat of mixing, it would seem a logical procedure to compare it with some relatively small, closely related heat effect, such as the heat of dilution. For example, one might compute the heat of mixing of a given number (s_A) of strions of solute A ($\mu = \mu_1$) with a solution of solute B ($\mu = \mu_1$) containing a given number (k_B) of kilograms of water, and compare this with the heat of diluting s_A strions of solute A ($\mu = \mu_1$) with k_B kilograms of water. This is the procedure followed.

The most significant region of concentration in which to compare the heat of mixing and the heat of dilution is the dilute region since it is there that our predictions concerning the magnitudes of heats of mixing can be put to the severest test and since the heats of dilution of many salts are well known in this region. For the present we will restrict ourselves to the region $0 < \sqrt{\mu} \leq 0.2$. We write:

$$0.8 \text{ str. NaCl}(\mu=\mu_1) + 0.2 \text{ str. Na}_2\text{SO}_4(\mu=\mu_1) = 1 \text{ str. Mixt.}(\mu=\mu_1);$$

$$\Delta H = \Delta H(\text{Mix.}) = Q = -7.4 \mu_1 \text{ (see eq. (70)).} \quad (74)$$

$$0.8 \text{ str. NaCl}(\mu=\mu_1) + \frac{0.2}{\mu_1} \text{ kg. H}_2\text{O} = 0.8 \text{ str. NaCl}(\mu=0.8\mu_1);$$

$$\Delta H = \Delta H(\text{Dil.}) = 0.8 \Delta \phi_s H = 0.8 \sigma \Delta \sqrt{\mu}. \quad (75)$$

Now $\sigma(\text{NaCl})$ is given approximately by the relation

$$\sigma = 477 - 1532\sqrt{\mu}, \quad (76)$$

from Young and Seligmann's¹⁶ equation (28). We also have (approximately):

$$\Delta \sqrt{\mu} = \frac{\Delta \mu}{2\sqrt{\mu}} = \frac{-0.2\mu_1}{2\sqrt{0.9\mu_1}} = -0.105\sqrt{\mu_1}. \text{ Hence,} \quad (77)$$

¹⁶Loc. cit.

$$\Delta H(\text{Dil.}) = 0.8(-0.105\sqrt{\mu_1})(477 - 1532\sqrt{0.9\mu_1}) = -40.2\sqrt{\mu_1} + 123\mu_1. \quad (78)$$

$$\frac{\Delta H(\text{Mix.})}{\Delta H(\text{Dil.})} = \frac{-7.4\mu_1}{-40.2\sqrt{\mu_1} + 123\mu_1} = \frac{0.060\sqrt{\mu_1}}{0.327 - \sqrt{\mu_1}} \quad (79)$$

For $0 < \sqrt{\mu_1} \leq 0.2$, this ratio has its largest value at $\sqrt{\mu_1} = 0.2$, namely, 0.095. That is, the heat of mixing at $\sqrt{\mu_1} = 0.2$ is only one-tenth as large as the heat of dilution. As $\sqrt{\mu_1}$ decreases from 0.2, the ratio becomes continually smaller and

$$\sqrt{\mu_1} \xrightarrow{L} 0 \quad \frac{\Delta H(\text{Mix.})}{\Delta H(\text{Dil.})} = 0. \quad (80)$$

The result is similar when the heat of mixing of solutions containing the same two solutes in an arbitrary proportion is compared with the corresponding heat of dilution of the NaCl or with that of the Na_2SO_4 . If, furthermore, we postulate (as seems reasonable) that for any pair of proper solutes, the derivative $(\frac{\partial Q}{\partial \mu})_S$ has a finite limiting value (as is the case for the solute-pair NaCl, Na_2SO_4), then we can easily show by generalizing the above argument that in sufficiently dilute solutions, the heat of mixing of solutions of any two solutes is much smaller in magnitude than the corresponding heat of dilution.

The results of the comparison are not as conclusive for concentrated solutions. Thus, for most solutes the heat of the short-chord dilution passes through zero somewhere in the moderately concentrated region, whereas the heat of mixing, increasing in absolute magnitude as the ionic strength increases, apparently never vanishes. If, however, we again restrict ourselves to a properly chosen concentration range, one in which σ does not vanish, the comparison is useful. Thus, it is found that for $\mu \geq 1$, the heat of mixing of NaCl and Na_2SO_4 at equal ionic strengths is never greater in absolute magnitude than 1/5 the corresponding heat of dilution of either salt. On the other hand, the heat of mixing of NaCl and HCl at $\mu = 1$, and also that of NaCl and LiCl at $\mu = 1$, is of the same order of magnitude as the corresponding heat of dilution. These are exceptional cases, however.

Comparison of Heats of Mixing of Solutions of the Same Concentration, the Concentration Being Expressed in Various Ways

In comparing the heats of mixing of solutions of the same concentration, we shall proceed to calculate the heats of mixing

for the different ways of expressing the concentration, employing in these calculations heat of dilution data and heats of mixing at equal ionic strengths. We shall limit our discussion for the present to the solute-pair $\text{NaCl}, \text{Na}_2\text{SO}_4$. Since these solutes belong to different valence types, they are especially suitable.

For the comparison in the important concentration region of the very dilute solution, it will suffice to compute the heat of mixing of two solutions of unequal ionic strengths, the exact nature of the relation between the ionic strengths not being specified. Restricting ourselves to the range $0 < \sqrt{\mu} \leq 0.2$, we add the following equations:

$$0.5 \text{ str. NaCl}(\mu_A) = 0.5 \text{ str. NaCl}(\mu); \quad \Delta H = \Delta H(\text{Dil. A}). \quad (81)$$

$$0.5 \text{ str. Na}_2\text{SO}_4(\mu_B) = 0.5 \text{ str. Na}_2\text{SO}_4(\mu); \quad \Delta H = \Delta H(\text{Dil. B}). \quad (82)$$

$$0.5 \text{ str. NaCl}(\mu) + 0.5 \text{ str. Na}_2\text{SO}_4(\mu) = 1 \text{ str. Mixt.}(\mu); \\ \Delta H = -12 \mu \quad (\text{see eq. (71)}). \quad (83)$$

$$0.5 \text{ str. NaCl}(\mu_A) + 0.5 \text{ str. Na}_2\text{SO}_4(\mu_B) = 1 \text{ str. Mixt.}(\mu); \quad \mu_A \neq \mu_B; \\ \Delta H = \Delta H(\mu_A \neq \mu_B) = \Delta H(\text{Dil. A}) + \Delta H(\text{Dil. B}) - 12 \mu. \quad (84)$$

For $\sqrt{\mu} < 0.2$:

$$\sigma(\text{NaCl}) = 477 - 1532 \sqrt{\mu} \quad (\text{see eq. (76)}).$$

$$\sigma(\text{Na}_2\text{SO}_4) = 477 - 1728 \sqrt{\mu}, \quad (85)$$

the latter equation being derived from Young and Seligmann's¹⁷ equation (45).

$$\Delta H(\text{Dil. A}) = \frac{1}{2} \sigma_{\text{Mean}} \Delta \sqrt{\mu} = \frac{1}{2} [477 - 1532 \left(\frac{\sqrt{\mu} + \sqrt{\mu_A}}{2} \right)] (\sqrt{\mu} - \sqrt{\mu_A}). \quad (86)$$

$$\Delta H(\text{Dil. B}) = \frac{1}{2} [477 - 1728 \left(\frac{\sqrt{\mu} + \sqrt{\mu_B}}{2} \right)] (\sqrt{\mu} - \sqrt{\mu_B}). \quad (87)$$

$$\Delta H(\mu_A \neq \mu_B) = -477 \left[\frac{1}{2} (\sqrt{\mu_A} + \sqrt{\mu_B}) - \sqrt{\mu} \right] - 383(\mu - \mu_A) - 432(\mu - \mu_B) - 12\mu. \quad (88)$$

Let $\mu_A = r\mu$ and $\mu_B = s\mu$. Since μ_A, μ_B , and μ satisfy the relation $\frac{1}{\mu} = \frac{.5}{\mu_A} + \frac{.5}{\mu_B}$, r and s must satisfy the equation $\frac{1}{r} + \frac{1}{s} = 2$. Also, r and s must satisfy the inequalities $r > 1/2$, $s > 1/2$; and $r \neq 1$, $s \neq 1$.

$$\Delta H(\mu_A \neq \mu_B) = -477 \left[\frac{1}{2} (\sqrt{r} + \sqrt{s}) - 1 \right] \sqrt{\mu} - 383(1-r)\mu - 432(1-s)\mu - 12\mu. \quad (89)$$

$$= -477 \left[\frac{1}{2} (\sqrt{r} + \sqrt{s}) - 1 \right] \sqrt{\mu} + (383r + 432s - 827)\mu. \quad (89a)$$

¹⁷Loc. cit.

We now focus our attention on the quantity

$$f(r) \equiv \frac{1}{2}(\overline{r^2} + r^2)^{-1} - \frac{1}{2}(\overline{r^2} + \frac{\overline{r^2}}{\sqrt{\overline{r^2} - 1}})^{-1} \quad (80)$$

We set $v = \sqrt{\overline{r^2} - 1}$; then $v > 0$ and $v \neq 1$.

$$v^2 = \overline{r^2} - 1; \quad (81)$$

$$r = \frac{v^2 + 1}{2} \quad (81a)$$

$$f(r) = \frac{1}{2} \left[\frac{v^2 + 1}{2} (1 + \frac{1}{v}) \right]^{-1} - \frac{1}{2v} \left[\frac{v^2 + 1}{2} (v + 1) - 2v \right]^{-1} \quad (82)$$

To prove that $f(r) > 0$, we proceed as follows:

$$(1 - v^2)^2 + 2v(1 - v)^2 > 0. \quad (83)$$

$$(1 - 2v^2 + v^4) + 2v(1 - 2v + v^2) > 0.$$

$$(1 + 2v^2 + v^4) + 2v(1 + 2v + v^2) > 8v^2$$

$$(1 + v^2)^2 + 2v(1 + v)^2 > 8v^2$$

$$\left(\frac{1 + v^2}{2}\right)(1 + v^2 + 2v) > 4v^2$$

$$\sqrt{\frac{1 + v^2}{2}}(1 + v) > 2v, \quad \text{whence } f(r) > 0.$$

We set

$$F(r) = -4\pi^2 f(r), \quad (84)$$

$$G(r) = 888r + 432s - 827. \quad (85)$$

The expression becomes:

$$\Delta H(\mu_A \approx \mu_B) = F(r)(\overline{\mu} + G(r)\mu), \quad \text{with } F(r) < 0. \quad (86)$$

We now specify that r be independent of μ .

$$\frac{\Delta H(\mu_A \approx \mu_B)}{\Delta H(\mu_A \approx \mu_B)} = \frac{-4\pi^2 \mu}{F(r)(\overline{\mu} + G(r)\mu)} = \frac{-4\pi^2 \sqrt{\overline{r^2}}}{F(r) + G(r)\sqrt{\overline{r^2}}} \quad (87)$$

If a sufficiently small value of $\sqrt{\overline{r^2}}$ is chosen, this ratio can be made arbitrarily small in absolute magnitude. We are led to the conclusion that in sufficiently dilute solutions, the heat of mixing at equal ionic strengths is much smaller in magnitude than the heat of mixing at unequal ionic strengths, regardless of the values of these ionic strengths. This seems that in very dilute solution, the heats of mixing at equal concentrations are smallest when the concentration is expressed as ionic strength. Of course, various other concentration terms may lead to small heats of mixing; but if they do, it is because the ionic strengths are

also equal. Thus, if the volume ionic strengths (ionic strengths on a volume basis) of dilute solutions of two solutes are equal, the weight ionic strengths are also equal; and in case the two solutes belong to the same valence type, the ionic strengths are equal if the molalities, molarities, mol fractions, or normalities are equal. On the other hand, the ionic strengths are never equal when the weight per cents are equal. These same conclusions are valid when the strion fraction of the mixture has values other than one-half, and are likewise valid for any solute-pair, provided the assumption is made that the derivative $(\frac{\partial Q}{\partial \mu})_S$ has a finite limiting value for that solute-pair.

The results of the comparison are not as conclusive in concentrated solutions. Thus, for mixings of NaCl and Na₂SO₄ in which the strion fraction and ionic strength of the final solution are 1/2 and 1, respectively, it is found that $|\frac{\Delta H}{S}| \leq 7$ if $-0.53 \leq \mu_B - \mu_A \leq 0.71$. That is, the ionic strengths of the two solutes may differ by as much as 0.71 units, and yet the heat of mixing will be no larger in magnitude than the heat of mixing at equal ionic strengths. In fact, the heat of mixing vanishes for $\mu_B - \mu_A = -0.34$ and also for $\mu_B - \mu_A = 0.55$. Because of this rather wide range of ionic strength difference associated with small heats of mixing, it happens that the heat of mixing of solutions of NaCl and Na₂SO₄ is smaller in magnitude when the solutions are of the same normality than when they are of the same ionic strength, the ionic strength of the final solution being unity in each case. The heat of mixing at unit final ionic strength is also small when the solutions are of the same weight per cent. For a solute-pair chosen at random, the difference of the ionic strengths for equal normalities or for equal weight per cents, and therefore the corresponding heat of mixing, might be either very large or very small, depending primarily upon relations among the equivalent weights and strionic weights of the two solutes. For NaCl and Na₂SO₄ and for unit final ionic strength, the heat of mixing at equal molalities, mol fractions, or molarities is about five times as great as the heat of mixing at equal ionic strengths; the heat of mixing at equal volume ionic strengths differs but slightly from the heat of mixing at equal weight ionic strengths, the weight basis being preferred since it is much more convenient experimentally. In general, then, the most satisfac-

tory method of expressing concentration when dealing with heats of mixing is by means of the weight ionic strength.

Correlation of Heats of Mixing with Properties of the Solutes and Ions

In studying the relations among the heats of mixing for different solute-pairs, we shall confine ourselves to unit ionic strength, noting that the heats of mixing are sufficiently large at this concentration to permit their determination with enough precision for our present purpose, and also that the number of solutes which are sufficiently soluble to form aqueous solutions of unit ionic strength is large.

The $\mu = 1$ curves for the three solute-pairs thus far studied resemble each other in form, but they exhibit varying degrees of dissymmetry about the $S = 0.5$ axis. To make possible a quantitative comparison of the forms of heat of mixing curves, we determine new curves that are symmetrical by substituting for each ordinate $Q(S_A = r)$ the arithmetic average of the two ordinates $Q(S_A = r)$ and $Q(S_B = r)$. We define the mean heat of mixing for the solute-pair A,B at the composition $S_A = r$ as:

$$Q_M(S_A = r) = \frac{Q(S_A = r) + Q(S_B = r)}{2} = Q_M(S_B = r) = Q_M(S = r) = Q_M(S = 1 - r). \quad (98)$$

The forms of the Q_M curves are conveniently compared by the calculation and comparison of values of the ratio $\frac{Q_M(S=r)}{Q_M(S=.5)}$ for the different solute-pairs, r being permitted to assume first one round value, then another. The values of $Q(S_A = r)$ and $Q(S_B = r)$ were read from the plots of Figs. 1, 3, and 5. The results of the calculations are shown in the following table.

TABLE VI -- $\frac{Q_M(S=r)}{Q_M(S=.5)}$

Solute-Pair	$r = .1$	$r = .2$	$r = .3$	$r = .4$
NaCl, Na_2SO_4	.359	.636	.836	.957
NaCl, KCl	.355	.636	.836	.958
NaCl, LiCl	.362	.643	.843	.960
Relative Discrepancy	.019	.011	.008	.003

The maximum discrepancy observed between the results for any two solute-pairs at a round value of r is less than 2%. Hence, the Q_M curves for the three solute-pairs are approximately of the same shape, being nearly carried into one another by simple elongations or compressions. It is, therefore, possible to represent the heat of mixing of two mono-solute solutions at unit ionic strength, if the given solute-pair behaves "normally," by a particular ordinate of the Q_M curve (that is, by the value of Q_M at some fixed composition S). We define the characteristic heat of mixing $Q_C(A,B)$ for the solute-pair A,B as the mean heat of mixing at the composition $S = 0.1$ (and at unit ionic strength). Symbolically,

$$Q_C(A,B) = Q_M(S=0.1) = \frac{Q(S_A = 0.1) + Q(S_B = 0.1)}{2} \quad (99)$$

The composition $S = 0.1$ was selected to make possible the determination of the characteristic heat of mixing of a given solute-pair after only two experiments, thus permitting the investigation of a larger number of solute-pairs in a given time than would otherwise be possible. The characteristic heats of mixing for the different solute-pairs investigated are assembled in the following table:

TABLE VII -- $\mu = 1$

Solute-Pair	$Q(S_A = .1)$	$Q(S_B = .1)$	Q_C
NaCl, Na_2SO_4	- 2.64	- 2.23	- 2.43
NaCl, KCl	- 3.44	- 3.40	- 3.42
NaCl, LiCl	8.14	7.17	7.65
NaCl, HCl	12.69	10.69	11.69
KCl, LiCl	- 5.98	- 5.55	- 5.76
KCl, Na_2SO_4	- 0.36	0.65	
NaCl, NaBr	0.29	0.28	0.28
NaCl, NaNO_3	1.01	1.22	1.11
KCl, NaNO_3	-36.45	-35.72	-36.08
NaCl, KNO_3	27.17	29.85	28.51
KCl, NaBr	- 6.67	- 6.81	- 6.74

One generalization based on these limited data is that for a solute-pair having a common ion, the heat of mixing is

larger numerically when the differing ions are positive than when they are negative. Evidently, different negative ions resemble one another to a greater degree than different positive ions resemble each other, as far as heats of mixing are concerned. Bernal and Fowler¹⁸ have shown from density measurements that, aside from OH^- and F^- , all negative ions are alike in that they are not hydrated, whereas the positive ions other than Rb^+ and Cs^+ are all hydrated to a greater or lesser degree. These facts suggest that the heat of mixing of two solutes containing a common ion may be dependent upon the difference in the degrees of hydration of the differing ions, the numerical value of the heat of mixing being large when this difference is large numerically, etc.

Apparently, no simple relation exists among the heats of mixing of the chlorides of the alkali metals. The two heats of mixing largest numerically both involve the chloride of lithium. The element lithium stands out among the alkali metals, its peculiar properties deriving from the fact that the lithium ion is so much smaller than the ions of the other alkalis. Presumably, this difference in ion size, leading to a difference in degree of hydration, is responsible for the heat of mixing of the chlorides of two alkali metals.

In general, experiments in which the members of the solute-pair contain no ion in common are apt to give results that are strikingly different from the results of experiments in which the solutes have a common ion. Thus, the constant- μ curve for the pair KCl , Na_2SO_4 differs radically in form from the curves of all other solute-pairs. This curve is apparently S-shaped, having positive ordinates at one end and negative ordinates at the other, and crossing the $Q = 0$ axis at some intermediate point. Because of this abnormality, no value of Q_c is given in Table VII for this solute-pair.

The heat of mixing of NaBr and KCl is about twice as large numerically as the heat of mixing of NaCl and KCl . This result is not surprising; we would expect the heat of mixing to be larger when the four ions are different than when two of them are the same since the changes in the environments of the ions during the mixing are more extensive in the former case than in the latter.

¹⁸Bernal and Fowler, J. Chem. Phys., 1, 515-48 (1933).

However, the heat of mixing of KCl with NaNO_3 and the heat of mixing of NaCl with KNO_3 , whose signs oppose each other, are abnormally large compared to the heat of mixing of NaCl with NaNO_3 and the heat of mixing of NaCl with KCl. These facts suggest that the apparently anomalous results are ascribable to the nitrate ion, the latter being unusual in its adjustment to the fields of the positive ions.

Further evidence of the anomalous behavior of the nitrate ion was obtained in this laboratory by Dr. Simon Freed and his co-workers.¹⁹ They found that the structure of the absorption spectrum of the europium ion, which represents the structure of the field about the ion, is practically the same in aqueous solutions of EuCl_3 , EuBr_3 , and $\text{Eu}(\text{ClO}_3)_3$, but that the spectrum of the europium ion in all solutions of $\text{Eu}(\text{NO}_3)_3$ except very dilute ones possesses a structure rarely observed in solutions of europium salts. Yet, the salts of europium, including the nitrate, are strongly dissociated electrolytes.²⁰ Thus, nitrate ion is exceptional among the univalent negative ions studied in its effect upon the environment of the europium ion in solution.

If the nitrate ion can exert a decidedly different and powerful effect upon the spectrum of the europium ion, and therefore upon the incompletely filled inner electron shell, which is shielded by two completely filled outer shells, one would expect the nitrate ion to exert large effects upon the fields of such positive ions as Na^+ and K^+ . Thus, when NaNO_3 is mixed with KCl, in which process nitrate ions pass from the neighborhoods of sodium ions to those of potassium ions, one is not surprised to find an energy change of much larger magnitude than the energy change which occurs when the solutions mixed contain univalent negative ions other than nitrate ions. Heats of mixing, therefore, are consistent with conclusions drawn from absorption spectra.

Structurally, the nitrate ion differs from the other univalent negative ions in that it possesses a planar configuration. This planar configuration is largely responsible, it is to be ex-

¹⁹(a) Freed and Weissman, *J. Chem. Phys.*, **6**, 297 (1938); (b) Freed and Jacobson, *J. Chem. Phys.*, **6**, 654 (1938); (c) Freed, Weissman, Fortess, and Jacobson, *J. Chem. Phys.*, **7**, 824 (1939).

²⁰I. M. Klotz, *J. Chem. Phys.*, **6**, 907 (1938).

pected, for the extraordinary polarizing power of the nitrate ion, enabling it to exert an unusual effect upon electric fields in the environments of positive ions.

SUMMARY

A knowledge of the heats of mixing of aqueous solutions of non-reacting strong electrolytes of the same ionic strength is important: first, because certain of these heats of mixing are encountered in the calculation of thermodynamic quantities from calorimetric data; and, second, because such a knowledge may throw some light on the nature of electrolytic solutions. By means of an apparatus designed for heat of dilution experiments, heats of mixing were determined for several solute-pairs.

For NaCl and Na₂SO₄, heats of mixing were determined at ionic strengths of 0.2, 0.5, 1, 2, and 5 and at solute-fractions covering the entire range from 0 to 1. The ΔH of mixing, always negative (heat being evolved), is greatest numerically for large ionic strengths and for large solute-fractions, decreasing rapidly when either variable is decreased. When solutions of NaCl and Na₂SO₄, each of unit ionic strength and containing 500 grams of water, are mixed at 25°, 6.8 calories are liberated. The constant- μ curves (in which ΔH of mixing is plotted against solute-fraction) are nearly parabolas at $\mu = 0.2$ but show pronounced dissymmetry as the ionic strength increases. When the heat of mixing at a fixed solute-fraction is plotted against the ionic strength, the slope of the curve is found to approach a finite value as the ionic strength approaches zero. From this result, it is shown that in sufficiently dilute solutions, the heat of mixing at equal ionic strengths is much smaller numerically than the heat of mixing at unequal ionic strengths (for example, the heat of dilution).

For NaCl and KCl, and also for NaCl and LiCl, heats of mixing were determined at unit ionic strength and at solute-fractions covering the entire range from 0 to 1. For NaCl and KCl, the ΔH 's of mixing are all negative (heat is evolved) and the curve (ΔH of mixing against solute-fraction) resembles that of NaCl and Na₂SO₄ for $\mu = 1$. For NaCl and LiCl, the ΔH 's of mixing

are all positive (heat is absorbed). If the curve were reflected through the $\Delta H = 0$ axis, it would then resemble in form the curve of NaCl and Na_2SO_4 for $\mu = 1$; but its ordinates are three times as large numerically.

For each of several solute-pairs, a few heats of mixing were obtained at unit ionic strength. These few data were enough to permit the determination of a "characteristic heat of mixing," C , for each solute-pair. A comparison of values of C for the different solute-pairs discloses some interesting facts. The curve for the pair KCl, Na_2SO_4 differs radically from the curves of all other solute-pairs, being S-shaped instead of parabolic. $C(\text{NaCl}, \text{NaNO}_3)$ and $C(\text{NaCl}, \text{KCl})$ are both small, whereas $C(\text{KCl}, \text{NaNO}_3)$ is abnormally large and opposite in sign to $C(\text{NaCl}, \text{KNO}_3)$, which is also large. It is concluded that experiments in which the members of the solute-pair contain no ion in common are apt to give results that are strikingly different from the results of experiments in which the solutes have a common ion. Another interesting fact is that in each case of the mixing of solutes having a common ion, C is larger numerically when the differing ions are positive than when they are negative.

